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REPORT DRXTH-TE-CR-83211

DEVELOPMENT OF NOVEL DECONTAMINATION AND INERTING
TECHNIQUES FOR EXPLOSIVES CONTAMINATED FACILITIES

Phase I - Identification and Evaluation of
Novel Decontamination Concepts

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JULY, 1983

TASK FINAL REPORT FOR THE PERIOD MAY 1982 TO FEBRUARY 1983
VOLUME I OF TWO VOLUMES

$T\mathcal{E}$

Prepared for:

U. S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY
ABERDEEN PROVING GROUND, MARYLAND   21010

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Explosives	Inerting Concepts	Field Surveys	Structures	Reductents
TNT, DNT, RDX	Decontamination Concepts	Nitroglycerin	Thermal	Hot Gases
HMX, Tetryl	Installation Restoration	Nitrocellulose	Facilities	Solubilization
Physical	Solvent Extraction	Nitroquanadine	Concrete	Steam
Chemical	White Phosphorus	Hydroblast	Painted	Steel Bases

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
Study identified and evaluated novel methods for the decontamination and inerting of facilities (buildings and equipment) contaminated with explosives during manufacturing or demilitarization. First step entailed review of literature and industrial survey followed by idea generation and detailed concept development. In the second step, criteria to evaluate the concepts were developed and covered, Mass Transfer, Destruction Efficiency, Safety, Damage to Buildings, Penetration Depth, Applicability to Complex Surfaces, Operating Costs, Capital Costs and Waste Treatment Costs. Thirdly these criteria were used to select promising

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concepts from about 55 concepts for evaluation in a follow on laboratory eval-
uation. Concepts recommended for experimental evaluation in the second phase
of the program were hot gases, vapor circulation, and chemical methods involv-
ing radical or base initiated decomposition and the use of reductants such as
sulfide or borohydride ions. Solubilization of explosives will be an important
aspect in the development of chemical methods

EXECUTIVE SUMMARY

As part of their responsibilities in DOD real property disposal, USATHAMA must identify, contain and eliminate toxic and hazardous materials and related contamination where lands and facilities, potentially available for alternate government or private use, have been declared excess or are candidates for excessing. With this mandate USATHAMA is to provide the technical basis to implement the decontamination and also provide the standards to insure decontamination has been effective. The Novel Processing Technology Program is to identify and develop treatment methods and recommend plans for carrying out the decontamination. The ideal concept would be a single method that is both universally applicable and most cost effective. Decontamination of structures and equipment contaminated with various explosives and related chemicals to a level that doesn't pose a hazard during unrestricted use, represents an extremely difficult problem in any excessing action. Under special conditions inerting the explosives may prove to be adequate so that the building can be demolished safely.

The objective of this research and development program on Novel Processing Technology is to identify, evaluate and develop novel techniques to decontaminate or inert Army installation structures, i.e. buildings and their contents, contaminated with explosives.

In this first phase study about 55 concepts were generated and described in sufficient detail to permit their evaluation against the criteria of mass transfer, destruction efficiency, safety, damage to structures, penetration depth, applicability to complex structures, operating costs, capital costs, and waste treatment costs. This evaluation was the basis for the selection of the most promising concepts for experimental evaluation in the second phase laboratory studies. The most promising concepts recommended for evaluation were the use of hot gases, vapor circulation and five chemical methods, involving radical or base initiated decompositions and the use of reductants. The Phase II effort will be designed to evaluate and recommend one to three of the concepts for field evaluation with the objective of addressing the program's overall plan of determining whether a single method can be universally applicable and cost effective.

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TASK 2

on

DEVELOPMENT OF NOVEL DECONTAMINATION AND
INERTING TECHNIQUES FOR EXPLOSIVES
CONTAMINATED FACILITIES - PHASE I

Contract DAAK11-81-C-0101

to

UNITED STATES ARMY
Toxic and Hazardous Materials Agency

from

BATTELLE
Columbus Laboratories

July 7, 1983

1.0 INTRODUCTION

The United States Army envisions that new, improved procedures
for the decontamination of facilities previously utilized for chemical
explosives manufacture or testing are now or will be required in the
future. The only currently approved method of decontaminating materials
involves incineration at a temperature of 1000 F for a period of 15 min-
utes. Materials exposed to such conditions are described as having at-
tained the 5X status and are defined as suitable for unrestricted use.
Unfortunately, the time and expense required to accomplish such decontam-
ination is immense. Successful development of an alternative decontam-
ination technique which would not require the dismantling of a facility
and which would result in a 5X decontamination status rating (or its

equivalent) without incineration represents a potentially large cost savings to the Government.

Examples of installations which might require such decontamination include Sunflower Army Ammunition Plant, Joliet Army Ammunition Plant, and Louisiana Army Ammunition Plant. Of concern in these facilities are building structures, underground and above ground storage tanks, reaction vessels, sumps, waste stream conduits, and pipes. Both the surface of the material and the interior areas into which explosives have penetrated require decontamination.

Also of interest to the Government is the inerting of explosives in contaminated buildings to allow the structures to be safely demolished and/or dismantled. This approach is particularly useful when a building to be demolished is located close to other remaining facilities and care must be taken to avoid an explosion or fire which might spread to these buildings.

2.0 OBJECTIVE

The objective of Phase I of Task 2 is to identify and evaluate the technical feasibility of novel decontamination and inerting concepts for explosives contaminated facilities.

2.1 CONTAMINATION SCENARIO

The United States Army Toxic and Hazardous Materials Agency (USATHAMA) has identified eleven explosives as the focus of the decontamination effort. These explosives are trinitrotoluene (TNT), dinitrotoluene (DNT), cyclonite (RDX), octagen (HMX), tetryl, nitroglycerin (NG), nitroguanidine (NQ), nitrocellulose (NC), ammonium nitrate (AN), lead azide, and lead styphnate. White phosphorous was also studied. The structure of each compound is shown below:

TNT:

NC:
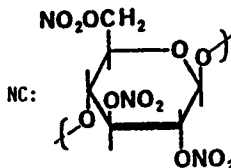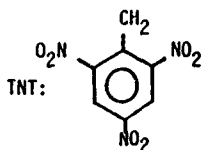
DNT: 2,4- AND 2,6- DINITROTOLUENE

NQ: $NH_2\overset{NH}{\overset{\|}{C}}-NHNO_2$

RDX:

TETRYL:

HMX:

LEAD AZIDE: $Pb(N_3)_2$

NG: $\overset{ONO_2}{\underset{}{C}}H\overset{ONO_2}{\underset{ONO_2}{C}}H_2\overset{}{C}H$

LEAD STYPHNATE:
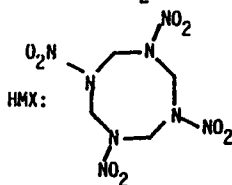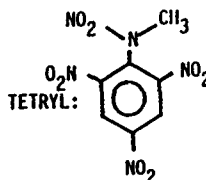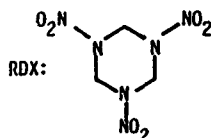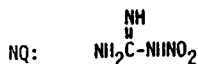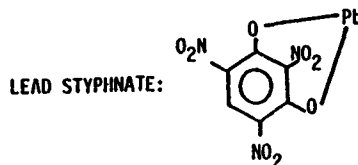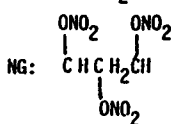
To ensure that unnecessary effort would not be devoted to building materials of only secondary importance, USATHAMA specified at the beginning of Task 2 that the substrates of principal interest were: (1) carbon steel, (2) stainless steel, (3) concrete, (4) tile, (5) brick, (6) cement, (7) wood, and (8) transite. These material were to be considered in both painted and unpainted condition.

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2.2 THE 5X "DILEMMA"

In order to satisfy the task objective, work during this phase consisted of three principal interrelated activities. The goal of the first activity was to identify novel decontamination and inerting methods. This was accomplished in three steps: (1) existing literature (both government, open literature and private) on decontamination and inerting procedures was thoroughly evaluated; (2) idea generation sessions were conducted to develop new decontamination and inerting concepts; and (3) a data base containing background information necessary for assessment of the chemistry and engineering aspects of new and existing concepts was developed.

The goal of the second activity was the development of evaluation criteria designed to evaluate and rank the concepts. The third activity involved the application of these criteria to the concepts in order to select the most promising candidates for experimental study in Phase II.

A dilemma arose in the execution of the second and third activities as a result of the fact that the desired level of decontamination specified by the tasking document was defined as the 5X condition. Since the 5X condition is an operational rather than an analytical definition, it does not provide a means to analytically evaluate the relative efficacy of novel decontamination concepts either in the preliminary screening or in subsequent laboratory testing. In fact, there appears to be little experimental documentation that the 5X condition actually accomplishes total decontamination, although our study indicates that such a conclusion is appropriate at least in the case of surface decontamination. So that we might have a more tangible criterion upon which we could evaluate novel decontamination concepts, we elected to define the reduction of contamination to a level below that detectable by state-of-the-art analytical techniques as constituting a successful decontamination.

3.0 RESOURCE REVIEW

There were four major sources of decontamination and inerting concepts in Task 2. Explosive manufacturers were contacted by phone to determine their current decontamination or inerting procedures. Idea generation sessions were held with Battelle staff to generate novel decontamination and inerting concepts. Both government and non-government publications were computer searched to uncover pertinent data for novel applications.

3.1 TELEPHONE SURVEYS

Twenty-four explosive manufacturers were contacted by phone to determine their decontamination methods. The list of companies was obtained from Thomas Register and is shown in Figure 1.

The following conclusions can be derived from the results of the survey:

- The primary clean-up method is either a water wash or a steam clean. The contaminated water is collected in a sump where the solids settle. Periodically, the solids are removed and burned in the open.

- The primary incentive for clean-up is to eliminate explosive hazards with little concern for the toxicity of the explosives.

- OSHA has no regulations regarding the hazards of toxic explosives.

APACHE POWDER COMPANY

CHEMTRONICS

AUSTIN POWDER COMPANY

IME

MONSANTO

BROCO, INC.

GULF EXPLOSIVES

HOLSTON AAP (KODAK)

TROJAN, INC.

TECHNICAL ORDNANCE, INC.

TELEDYNE McCORMICK SELPH

EXPLOSIVE TECHNOLOGY, INC.

JET RESEARCH CENTER

EXPRO CHEM LTD.

GOEX, INC.

INDIANA AAP (ICI)

DELAWARE POWDER COMPANY

TITAN EXPLOSIVES COMPANY

SECURITY SIGNALS, INC.

LFC CHEMICAL

HOLEX

EPA

WHITTAKER CORPORATION

OSHA

C.I.L., INC.

AIR PRODUCTS, INC.

FIGURE 1. AGENCIES AND EXPLOSIVES MANUFACTURERS CONTACTED

- There are no standard procedures for decontamination; the only widely used decontamination material is the nitro-glycerin killer, an aqueous solution of sodium sulfide, although alkalies are occasionally used to decompose HMX and RDX.

- Seldom are any chemical analyses done to determine the effectiveness of clean-up. A subjective visual method is almost always used.

The information obtained from the survey of explosive manufac-turers was summarized and distributed to the project team for review and incorporation into the program.

3.2 GOVERNMENT AND NON GOVERNMENT PUBLICATIONS

The literature was searched to identify pertinent data for app-lication to novel means of explosives decontamination and inerting. Both government and non-government publications were searched. These publica-tions are summarized in Figure 2. The government indices searched were: Smithsonian Science Information Exchange (SSIE), current research reports; National Technical Information Service (NTIS), unclassified re-search reports; Defense Technical Information Center (DTIC), defense-related classified and unclassified research reports; and Central Infor mation Reference and Control (CIRC), unclassified foreign defense-related reports.

The non-government indices searched were: Chemical Information System (CIS), a broad, chemical data base; Oil and Hazardous Materials (OHMTADS), part of CIS; Compendex, an engineering index; Comprehensive Dissertation Index (CDI), abstracts on dissertations; Applied Science and Technology Index (AS and TI), applications; Chemical Abstracts (CA),

GOVERNMENT PUBLICATIONS

- SSIE

- NTIS

- DTIC

- CIRC

NON-GOVERNMENT PUBLICATIONS

- CIS

- OHMTADS

- COMPENDEX

- CDI

- CA

- AS AND TI

- EH AND PC

FIGURE 2. PUBLICATIONS SEARCHED

broad, chemical data base; and <u>Environmental Health and Pollution Control</u> (EH and PC), reports on pollution control.

The computer strategy used to search these publications was a cross-matching of specific and general explosives terms with specific and general chemical and engineering terms. This strategy is outlined in Figure 3 and elaborated upon below:.

- The specific explosives were TNT, DNT, RDX, HMX, tetryl, nitroglycerine, nitroguanidine, nitrocellulose, ammonium nitrate, lead styphnate, and white phosphorus. Any common name, registry number, trade name, or IUPAC name of the agents or explosives was also included in the search.

- The general explosive terms were explosives, propellants, initiators, primer, and pyrotechnics.

- The specific chemical reaction terms searched were reduction, oxidation, cleavage, substitution, coupling, elimination, hydrolysis, neutralization, gamma irradiation (radiation), ultraviolet, and extraction. The specific engineering terms used were diffusion, porosity, permeability, mass transfer, half-life, persistency, and semi-permeability.

- The general chemical process terms searched were decontamination, desensitization, demilitarization, aging, degradation, decomposition, destruction, chemical, thermal, microbial, enzymatic, and reviews.

The strategy described above was progressively structured after review of the resulting abstracts. Thus, not all publications were searched exactly according to this scheme—some were searched with a modified version.

SEARCH STRATEGY
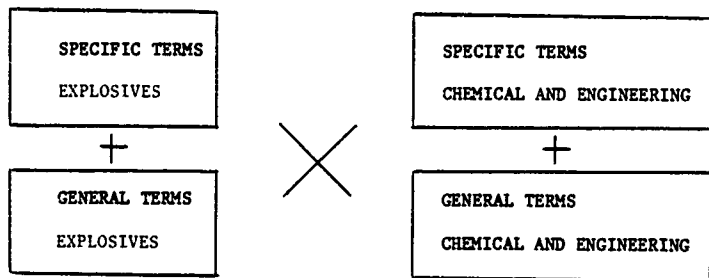
FIGURE 3.   SEARCH STRATEGY

The computer search of government and non-government publications resulted in approximately three thousand abstracts which were then processed as shown in Figure 4. In addition, Chemical Abstracts was manually searched between 1929 and 1967. These abstracts were reviewed by project team members and approximately a thousand of them were found pertinent to the present task. Each pertinent abstract received a reference number and was categorized according to subject matter, i.e., general, chemical, physical, thermal, biological, radiative, analytical, toxicological or general. It was then decided if a paper was to be ordered from the abstract or the abstract simply filed. As ordered papers were received, they were placed in a file in order of the abstract reference number.

All abstracts were placed in a "physical" file and a "computer" file was set up in parallel. This computer file consists of an 8 line entry for each abstract, listing 1) Reference number, 2) Author(s), 3) Category, 4) Title, 5) Reference, 6) Was a paper ordered?, 7) Abstracter's initials, and 8) Has the paper arrived? This system was very useful for pooling data on a specific agent under a certain category. For example, one could obtain a list of all references pertaining to the chemical decomposition of TNT by searching "chemical" and "TNT".

All of the abstracts in the "physical" file were distributed to staff and project team members according to the category or categories listed on each abstract.

3.3 IDEA GENERATION SESSIONS

Approximately 30% of the decontamination concepts identified in Phase I were the result of idea generation sessions. These sessions were arranged such that several individuals of specific disciplines met with project team chemists and engineers to "brainstorm" ideas for decontamination or inerting of explosives. The specific disciplines involved included organic chemists, biologists, explosives specialists, polymer

ORDERING, FILING AND DISTRIBUTION PROCEDURES
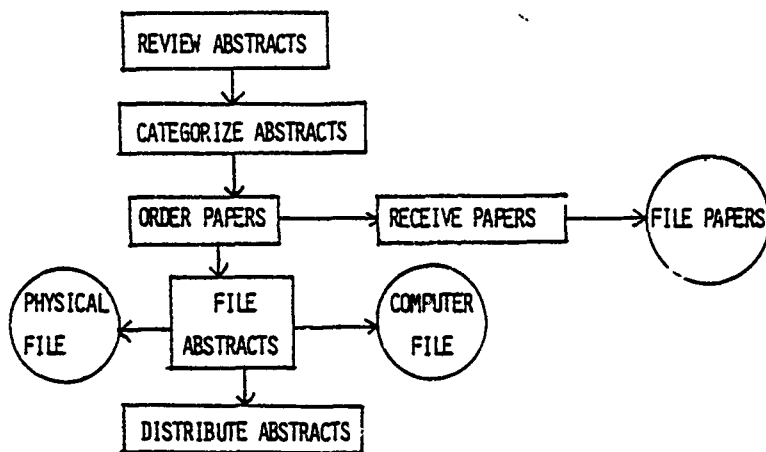
FIGURE 4. ORDERING, FILING, AND
DISTRIBUTION PROCEDURES

chemists, and experts in high energy radiation phenomena. A synergism in the formulation of ideas between project team members and specialists was evident in these sessions. The resulting ideas were developed into detailed concepts which were incorporated into the program.

4.0 CONCEPT DESCRIPTION

Armed with the data from the literature searches, idea generation sessions, and manufacturer's reports, a series of small groups composed of appropriate specialists met and attempted to evaluate all of the envisioned decontamination concepts. During this process it became obvious that the concepts we • inadequately described for a meaningful evaluation. Through a progressive design, a concept description format was developed which enabled the project team describe the concepts in reasonable detail. Once the description forms were completed, a normalized, meaningful evaluation could be performed.

The final concept description format can be found in Figures 5-8. The headings listed are, for the most part, self-explanatory. Those that need some explanation will now be addressed. The first section of the final format (Figure 5) the concept is described in general terms for easy reference including the obvious advantages and disadvantages. The second section deals with the specific chemical reactions and by-products anticipated. Supplementary treatment refers to any additional chemistry that must be invoked to remove by-products. The third section discusses aspects of a physical removal technique. Supplementary treatment in this context refers to additional chemical/physical procedures necessary to treat remaining contaminants. Waste treatment and disposal refer to procedures that must be performed before the waste could be disposed of.

The fourth section of the concept description format (Figure 6) deals with the applicability of the method to the contaminants and to the building materials and structural features. Secondary decontamination treatment refers to any procedure that must be performed to decontaminate

Concept Description Format

1.0 General Description

    1.1 Summary of idea

    1.2 Origination of idea

    1.3 Obvious advantages and disadvantages

    1.4 Variations of idea

    1.5 Sketch

2.0 Chemical Decomposition Treatment

    2.1 Chemical reactions(s)

    2.2 Hazardous products

    2.3 Destruction efficiency, residue level (relative to detection limits)

    2.4 Reaction rate/kinetics

    2.5 Supplementary treatment(s)

    2.6 State-of-the-art

3.0 Physical Treatment

    3.1 Removal efficiency, residue level (relative to detection limits)

    3.2 Hazardous wastes

    3.3 Supplementary treatment(s)

    3.4 Waste recovery and disposal

    3.5 State-of-the-art

FIGURE 5. PAGE 1 OF CONCEPT DESCRIPTION FORM

15

4.0 Applicability

  4.1 Explosive applicability
  4.2 Isolated building material applicability (concrete, tile, brick, cement, wood, steel, transite, painted and unpainted surfaces)

    4.2.1 Impact of substrate on chemistry
    4.2.2 Removal or reaction of contaminant from surface
    4.2.3 Removal or reaction of contaminant from interior
    4.2.4 Damage to material

  4.3 Practical applicability to building

    4.3.1 Building preparation (e.g., paint removal, water wash, barrier installation, necessary prior decontamination level)
    4.3.2 Practical physical limitations/methods to overcome (e.g., formulation of reagent, complex surface areas)
    4.3.3 Secondary decontamination treatment(s)
    4.3.4 Clean-up requirements (prior to paint)
    4.3.5 Waste treatment and disposal

  4.4 State-of-the-art

FIGURE 6. PAGE 2 OF CONCEPT DESCRIPTION FORM

5.0 Engineering

    5.1 Process description (e.g., block diagram)

        5.1.1 Main process
        5.1.2 Variations

    5.2 Equipment/support facilities needed

        5.2.1 Description
        5.2.2 RAM (reliability, availability, maintainability)

    5.3 Decontamination time

        5.3.1 Set-up (building and equipment preparation)
        5.3.2 Application time

            5.3.2.1 Personnel
            5.3.2.2 Decontamination
            5.3.2.3 Verification (analysis of building and waste
                      products)

        5.3.3 Tear-down time

            5.3.3.1 Equipment removal
            5.3.3.2 Clean-up

    5.4 Safety requirements

        5.4.1 Process hazards
        5.4.2 Personnel hazards
        5.4.3 Protective methods

FIGURE 7. PAGE 3 OF CONCEPT DESCRIPTION FORM

6.0 Economics

    6.1 Building damage--repair costs

    6.2 Developmental costs

    6.3 Treatment costs

        6.3.1 Utilities and fuel cost

        6.3.2 Equipment cost

        6.3.3 Material cost

        6.3.4 Manpower costs

7.0 Future Work Required

    7.1 Knowledge gaps

    7.3 Resolution

FIGURE 8. PAGE 4 OF CONCEPT DESCRIPTION FORM

parts of the building not previously decontaminated. Clean-up means cus-
todial or janitorial services needed. Waste recovery and disposal refer
to the final disposal of waste either via incineration, landfill or spec-
ial burial or storage.

The fifth section (Figure 7) discusses four aspects of engi-
neering: process; equipment; decontamination time; and safety require-
ments. The sixth section (Figure 8) outlines all costs involved. Section
7 was not originally provided for in the logic diagrams used to develop
this format, but has been included as a summary of the knowledge gaps
discovered in the process of completing the forms. Resolution of these
knowledge gaps is also addressed.

A three-step procedure was followed in the completing of the
description forms. Project team members chose concepts in their area of
expertise and researched any knowledge gaps found. The description forms
were then passed to a chemical engineer who completed engineering aspects
of the concept. In the third step the forms were sent to a project team
member who reviewed each form and added comments when pertinent. In this
way, description forms were more complete, uniform and unbiased than if a
single scientist completed the task.

There were several assumptions made when formulating concepts.
These are as follows:

- All surfaces are contaminated, i.e. ceilings, floors,
  walls, sumps, and equipment.

- Contaminants have penetrated into porous media.

- Site surveys established a baseline to describe realistic
  concepts.

For each concept waste treatment, waste disposal, and process variations
were addressed. Appendix III contains the detailed concept description
forms for each envisioned concept.

5.0 SURVEY RESULTS

5.1 INTRODUCTION

Both agent and explosive installations were surveyed by project team members. The survey was designed to define the types and characteristics of surfaces, materials, and structures which might require decontamination. This information, not available by any other route, has been be applied to the evaluation of various decontamination processes proposed in this study.

The survey covered five installations with detailed characterizations of over twenty individual structures. In some cases, the buildings characterized were considered representative of duplicate operations at the same facility, or operations at other installations built in the same time period using the same general building designs. The installations visited were: Edgewood Area of the Aberdeen Proving Grounds, Joliet Army Ammunition Plant, Sunflower Army Ammunition Plant, Rocky Mountain Arsenal, and Louisiana Army Ammunition Plant. The structures ranged f· ·m small frame buildings built in 1942 to large concrete and steel complexes built in the late 1970's. Contaminants included a variety of explosives, chemical warfare agents, and chemicals.

Candidate installations were nominated on the basis of published literature and information from Army and Battelle personnel who had recently visited various installations. Factors used in selecting sites for visits included age, contaminants, and status (active versus stand-by). Records Research Reports (accessed through the Project Officer) were reviewed to ensure that the desired information was not already available and to identify specific candidate operations and structures to focus the survey effort prior to the installation visit.

During each site visit, additional guidance was sought from operating personnel in the selection of structures to be surveyed. Fur-

ther discussion was sought from operating personnel with regard to opera-
tion objectives, operating conditions, and any specific circumstances re-
lating to decontamination. Survey activities included inspections, note-
taking, photography (when permitted), contamination measurements, and
examination of maps, plans, and engineering drawings.

The information obtained in the surveys was distributed to the
project team by internal trip reports which included photographs, draw-
ings, and discussions of operating conditions.

5.2 SUMMARY OF STRUCTURES, MATERIALS AND CONTAMINANTS

The range of surfaces, materials and contaminants defined by the
survey is summarized in the matrix in Table 1. It may be noted that some
materials predominate at various locations. For example, at Sunflower
AAP, frame structures built in the early 1940's contain a large proportion
of plywood paneling, while corresponding structures at Joliet AAP contain
a large proportion of transite paneling. The materials at Louisiana AAP
were much more varied because the currently operating LAP lines originally
constructed in the 1940's have been modified over the years using mater-
ials available at the time of the renovation.

The degrees of contamination observed varied over a wide range.
Most of the buildings surveyed were classified 3X but some were not de-
contaminated at all. Explosives contamination varied from no visible con-
tamination to obvious deposits of explosives in cracks or crevices.
Chemical contamination varied from no   visible to obvious contamination
stains, i.e., B-1 dye. Agent contamination varied from no contamination
detected, e.g. no GB by bubbler determinations, to detectable residual
odors, e.g., mustard. The structures surveyed exhibited a wide range of
designs and conditions. Designs varied from one room frame buildings from
the 1940's to multi-story, concrete and steel complexes built in the
1950's to late 1970's (e.g., the GB plant at RMA and the nitroguanidine
plant at Sunflower AAP). The condition of the structures observed varied

TABLE 1. SUMMARY OF SURVEY OF MATERIALS AND CONTAMINANTS

Building Material	NG	NC	TNT	DNT	Tetryl	Comp B	WP	B-1 Dye	GB	Mustard and Phosgene
Concrete	x	x	+●	+	+	●	oΔ	o	Δ	Δ
Concrete block (painted)	-	-	●	-	-	●	Δ	-	Δ	Δ
Concrete block (unpainted)	-	-	-	-	-	-	o	o	-	-
Brick (painted)	-	x	-	-	-	-	-	o	-	-
Terra Cotta*	-	x	+●	+	-	-	-	o	Δ	Δ
Steel (mild)	x	x	+●	+	+	●	oΔ	o	Δ	Δ
Steel (stainless)	x	x	-	-	-	-	-	o	Δ	Δ
Lead sheet	x	x	+	+	+	-	-	-	-	-
Monel sheet/pipe	x	x	-	-	-	-	-	-	Δ	Δ
Glass	-	-	+●	+	+	●	oΔ	o	Δ	Δ
Plexiglass	x	x	+	-	+	-	-	o	Δ	-
PVC	x	-	-	-	-	-	-	-	-	-
Linoleum	-	-	+	+	-	-	-	-	-	-
Asphalt tile	x	x	-	-	-	-	-	-	-	-
Asbestos**	x	x	+●	+	+	●	o	o	-	Δ
Transite	-	-	+●	+	+	●	o	o	-	-
Wood (painted)	x	x	+●	+	+	●	o	-	-	Δ
Wood (unpainted)	-	x	+●	+	+	●	-	-	-	Δ

x = SAAP   + = JAAP   - = not present   ● = LAAP   o = Edgewood   Δ = RMA

* Includes pipe and/or block   NG = nitroglycerin   TNT = trinitrotoluene

** Sheet and/or insulation   NC = nitrocellulose   DNT = dinitrotoluene

WP = white phosphorus

widely depending on materials and climate, but principally on the state of
readiness or use. Frame structures from the 1940's varied most in condi-
tion. Some were in a state of ruin while others were freshly painted,
completely maintained, and in a state of high readiness.

The range of equipment within buildings varied over a similarly
wide range. Some buildings contained simple process tanks with a minimum
of pipes, wiring or ducting while others contained complex machine lines
with elaborate piping, steam ducts, conduit, wiring, and control
equipment.

In general, less thermal insulation was observed than expected
in typical industrial structures. Most frame structures contained no in-
sulation within the walls and a minimum of insulation on steam pipes
within the manufacturing areas. Some frame structures showed "inside-out"
design i.e. interior panels with framing exposed on the exterior of the
building.

5.3 CURRENT SITUATIONS

At Joliet AAP, a number of buildings have been designated for
scheduled excessing. Two major constraints were identified by installa-
tion personnel in terms of removal of some of the buildings. First, the
buildings to be excessed are adjacent to other buildings contaminated with
explosives. Second, the buildings to be excessed contain significant
amounts of transite (asbestos-base) paneling. It is projected that
"flashing", the present state-of-the-art explosives decontamination meth-
od, presents an explosion hazard in terms of the adjacent buildings and
"flashing" of these buildings presents a potential for uncontrolled emis-
sions of asbestos.

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5.4 IMPACT OF SURVEY FINDINGS

The survey findings established a range of materials for poten-
tial application of decontamination procedures. The results had most im-
pact on the study in terms of making evaluation criteria realistic. The
criteria were developed taking into account the reality of such factors as
multiple-coated or deteriorated paints, blind areas in structures, and the
complications presented by conduit and piping. The survey also inhibited
oversimplification of the goals and scope of this program.

The survey also identified a need to inert obsolete building and
equipment to a non-explosive state so that demolition of these buildings
could be safely performed. The survey results pointed to a need for such
alternatives to the present "5X/flashing" procedure for buildings. The
alternative need not be, however, a one-step process. Incremental mea-
sures which could be combined with routine dismantling steps might meet
the needs observed in current operations.

6.0 CRITERIA FOR EVALUATION

6.1 CONCEPT EVALUATION

In general, evaluation criteria were developed to aid in the
selection of methods for further development in Phase II. To make this
evaluation, seven general evaluation criteria were identified and des-
cribed in relation to the four concept categories: thermal, abrasive,
extractive, and chemical. It was determined that more meaningful evalua-
tion could be accomplished if the envisioned concepts were segregated ac-
cording to one of four categories. This eliminated inconsistencies
introduced, for example, when liquid chemical reagents would be compared
with physical abrasive methods. The better concepts in each category were
selected as a result of this segregation.

The decontamination concept criteria are presented in Table 2. For chemical treatments, two additional criteria were included, i.e. mass transfer and destruction efficiency. In order to consistently evaluate all the proposed methods a four-unit scoring system was developed in which a (++) rating was very good, a (+) was good, a (-) was poor, and a (--) was very poor. A four-unit system was chosen because it best reflected the accuracy of the evaluations. USATHAMA reviewed this system and found it to be satisfactory. The specific definitions of (++), (+), (-), and (--) as used in scoring are presented in Table 3. For chemical decontamination processes, the additional criteria and definitions of scoring are presented in Table 4. The definitions of the various ratings did not apply directly in all cases. When they did not apply, they were used merely as guides to obtain a normalized scoring.

The safety criterion refers to the inherent dangers present in implementing any concept.

The damage to building criterion indicates the effort needed to restore the building after decontamination. Repainting probably would be necessary even without decontamination, therefore, if repainting could repair treatment damage, the best rating (++) was given. The poorest rating (--) was given if the cost of restoration would be equivalent to the cost of a new building.

Penetration depth is difficult to define because of the wide variety of materials. Similarly, the penetration needed for decontamination is a knowledge gap. For example, a long-term thermal treatment from both sides of a wall should decontaminate completely through a structure and thus was given the best rating (++). Treatment with UV light would be expected to remove surface contamination only and thus was given the poorest rating (--). Treatment with a gas was given a (+) rating and treatment with a liquid was given a (-) rating if no unusual considerations made a different rating more appropriate.

Applicability to complex surfaces criterion addresses how well a method could be applied to areas such as behind piping and in corners.

TABLE 2. EVALUATION CRITERIA FOR BUILDING DECONTAMINATION

CRITERIA	THERMAL	PHYSICAL		CHEMICAL
		ABRASIVE REMOVAL	SOLVENT EXTRACTION	
Safety	Potential for burns, explosions, radiation exposure - poisoning	Potential for residual explosive detonation, dust, flying chips, noise	Flammability, toxicity, explosivity	Flammability, toxicity, explosivity, radiation exposure
Damage to Building	Damage resulting from thermal effects (cracking, dehydration, warping, fires, complete destruction)	Damage resulting from abrasive (rough surfaces requiring repair, complete destruction)	Corrosivity of solvent to metals, degradation of ceramics (wood, paint plastics are expendable)	Corrosivity of reactants to metals, degradation of ceramics (wood, paint, plastics are expendable)
Penetration Depth	Effective depth of thermal penetration	Effective depth of surface removal	Effective depth of solvent penetration	Effective depth of reactant penetration
Applicability to Complex Surfaces	Adaptability of heating equipment to complex areas in a building	Adaptability of abrasive equipment to complex areas in a building	Adaptability of solvent application equipment to complex areas in a building	Adaptability of reactant application to complex areas in a building
Operating Cost	Labor cost Materials cost Utilities costs Setup costs Cleanup costs	Labor cost Materials cost Utilities cost Setup costs Cleanup costs	Labor cost Materials cost Utilities costs Setup costs Cleanup costs	Labor cost Material cost Utilities cost Setup costs Cleanup costs
Capital Cost	Heating equipment, protective equipment	Abrasive equipment, protective equipment	Solvent application/ collection equipment	Reactant application/ collection equipment
Waste Treatment/ Recovery Cost	Hood, scrubbers, ash	Waste material requiring treatment incinerator	Solvent recovery equipment incinerator	Spent reactant treatment equipment incinerator

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TABLE 3. EVALUATION RATINGS FOR BUILDING DECONTAMINATION

CRITERIA	++	+	-	--
Safety	No hazards	Workmen in proximity of hot surfaces, projectiles, or require dust mask	Workmen in contact with hot surfaces, toxic materials, or require special protective clothing or breathing mask (org. vapor filter)	Workmen in building subject to collapse, or fire or explosion hazard is present or breathing apparatus is required.
Damage to Building	Requires only repainting	Requires cleanup Resurfacing	Requires major restoration	Demolished
Penetration Depth	Penetrates through building	Penetrates more than 1/8 in. into building material	Penetrates less than 1/8 in.	Surface removal only
Applicability to Complex Surfaces	Easy to cover all areas	Easy to apply behind piping	Difficult to apply behind piping-in corners	Flat walls only
Operating Cost	Minimal, equivalent to painting	Nominal, equivalent to plastering	Large, equivalent major restoration	Maximal, equivalent to rebuilding
Capital Cost	Nominal <$10,000	Low $10,000-$100,000	Moderate $100,000-$1,000,000	High >$1,000,000
Waste Treatment Cost	None	Conventional sewage or solid waste disposal	Conventional incineration or hazardous landfill	Special incineration or permanent storage

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TABLE 4. CRITICAL CHEMICAL PROCESS REQUIREMENTS FOR DECONTAMINATION

* Time for complete reaction is not specifically weighted.

Criteria	Criteria Definitions		
Mass Transfer	The nature of the effective contact between reagents and toxic compounds to permit the reactions to occur (solubility).		
Destruction Efficiency	A consideration of the degree of completion of the reaction and the toxicity of products.		
	++	+	−
Mass Transfer	Reagent and contaminant are miscible.	Reagent and contaminant are moderately soluble.	Either minimal solution.
			No solution.
Destruction Efficiency	Reacts to completion to produce non-toxic products.	Reacts to completion but products may be hazardous.	Less than total destruction.
			Low degree of reaction.

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The mechanical removal treatments generally scored low in this area while the application of liquid or gaseous reactants scored high.

Operating cost was a measure of expense of applying the treatment including set-up and tear-down. Except for one or two concepts in which expensive reagents were required, the major part of this cost was for manpower. The rating scale ranged from (++) for a cost equivalent to painting to (--) for costs equivalent to rebuilding.

Capital costs were the costs associated with purchasing equipment to apply the treatment. Equipment purchased as a capital cost would be reusable at another facility. Cost of disposable equipment was considered part of operating cost. The rating was based on order of magnitude ranges, from less than $10,000 which was scored (++), to more than $1,000,000 which was scored (--).

The waste treatment costs were those costs associated with disposal of debris, used chemicals, or washes. The best score (++) was given those processes which had no waste. If conventional landfill would be adequate, the concept was scored (+), if conventional incineration or a hazardous landfill would be required, the concept was scored (-), and if a special incinerator or permanent containerized storage would be required, the concept was scored (--).

Before any of the chemical concepts were evaluated under the seven criteria outlined above, they had to receive scores higher than (--) under the criteria of mass transfer and destruction efficiency. These two criteria were termed Critical Chemical Process Requirements. Mass transfer is a measure of the predicted effective contact between specific reagents and contaminants. Destruction efficiency refers to the combined measure of reaction efficiency and toxicity of the products. A method received a score of (++) if the reaction proceeds readily to completion (99.9%) and did not produce toxic products, and a score of (+) if the reaction went to completion but produced toxic products.

The scoring for the preliminary screening was made by a jury of three or four chemists and engineers who had studied the concept. The

score was arrived at by unanimous decision after the jury had discussed the other possible scores. It was understood at the outset that the limited range of scores and the lack of weighting factors limits the accuracy of this method of evaluating concepts. However, this method was adequate for recognizing the potentially best concepts and eliminating the poorer concepts.

The next step in the evaluation process consisted of summing the individual scores for each criterion. If a non-chemical concept had a total score of less than zero, it was eliminated. If a non-chemical concept scored a (--) in safety, penetration depth, or applicability to complex surfaces, it was also eliminated. If a non-chemical concept scored less than zero in the combined criteria of capital and operating costs, it was eliminated. The "surviving" non-chemical concepts were then subjected to a more rigorous engineering evaluation to determine if a method was feasible. Those concepts which were deemed feasible in terms of engineering were then subjected to a cost analysis which is outlined in Section 6.3. The better chemical concepts were then chosen on the basis of their total evaluation scores and potential in two areas: (1) the concept must score a (++) rating in the destruction efficiency criteria, and (2) the concept must be applicable to at least two or more explosives.

6.2 INFRTING CONCEPT EVALUATION

The criteria which were applied to the evaluation of inerting concepts were almost the same as those criteria applied to the evaluation of the decontamination concepts. However, the Damage to Building criteria was not applied to inerting concepts since the objective of inerting was to render an explosives contaminated building safe for demolition. The criterion termed Inerting Potential was utilized instead of the Destruction Efficiency criterion used for evaluation of decontamination concepts. The criteria and descriptions for inerting concepts are presented in Table 5. The specific definitions of (++), (+), (-), and (--) used in scoring

TABLE 5. EVALUATION CRITERIA FOR BUILDING INERTING

Criteria	Dissolution	Chemical
Mass Transfer	Solubility, wetting	Solubility
Inerting Potential	Desensitization, degree of reduced explosivity	Desensitization, degree reduced explosivity
Safety	Flammability, toxicity, explosivity	Flammability, toxicity, explosivity, radiation exposure
Penetration Depth	Effective depth of solvent penetration	Effective depth of reactant penetration
Applicability to Complex Surfaces	Adaptability of solvent application equipment to complex areas in a building	Adaptability of re-actant application to complex areas in a building
Operating Cost	Labor cost Materials cost Utilities cost Setup costs Cleanup costs	Labor cost Materials cost Utilities cost Setup costs Cleanup costs
Capital Cost	Solvent application/ collection equipment	Reactant application/ collection equipment
Waste Treatment/ Recovery Cost	Solvent recovery/ incinerator	Spent reactant treat-ment equipment incinerator

these concepts are presented in Table 6. A pre-screening approach using the Mass Transfer and Inerting Potential criteria was not followed in evaluating the inerting concepts.

6.3 COST EVALUATION

Concepts surviving the preliminary screening were evaluated on the basis of the cost of applying the concept. A detailed cost analysis can be found in Appendix II. To estimate the cost, a hypothetical explosives facility was assumed. The model facility was very small and any real facility will likely be several times as large. The hypothetical facility costed contains three buildings, each 60 feet long, 30 feet wide, and 25 feet high. One building is made of blast resistant concrete, 2 feet thick; one building is made of brick and mortar 12 inches thick; and one building is made of wood with 5/8 inch siding on both sides of 2x6 in studs. The floors of all buildings were assumed to be 1-foot thick concrete. The total weight of equipment, stairs, and pipes in the building is assumed to be 10 tons. The three buildings were assumed to be located close together.

6.4 FINAL EVALUATION

A guide to concepts evaluated in this task report is provided in Table 7. Only those physical and thermal concepts surviving initial, engineering, and cost analyses will be suggested for Phase II. Since the cost and engineering of most chemical treatments was essentially the same, those chemical decontamination and inerting concepts that scored highest in the evaluation procedure will be recommended for Phase II experimental verification studies. The final selection of chemical concepts for detailed experimental evaluation will be made after a brief laboratory screening in Phase II studies.

TABLE 6. BUILDING DESENSITIZATION EVALUATION RATINGS FOR BUILDING INERTING

Criteria	++	+	-	--
Mass Transfer	Reagent and contaminant are miscible. Penetrates materials well.	Reagent and contaminant are moderately soluble and reagent penetrates material moderately well.	Either minimal solution or minimal penetration.	No solution or penetration
Inerting Potential	Building is inerted by process.	Building is inerted if building pre-treated.	Building is desensitized but not inerted.	Building is not desensitized nor inerted.
Safety	No hazards	Workmen in proximity of hot surfaces, or require dust masks.	Workmen in contact with hot surfaces, toxic materials, or require special protective clothing or breathing mask	Workmen in building with toxic vapors or fire or explosion hazard is present, a breathing apparatus is required.
Penetration Depth	Penetrates through building.	Penetrates more than 1/8 inch into building material.	Penetrates less than 1/8 inch.	Surface removal only.
Applicability to Complex Surfaces	Easy to cover all areas	Easy to apply behind piping	Difficult to apply behind piping—in corners.	Flat walls only
Operating Cost	Minimal, equivalent to painting	Nominal, equivalent to plastering	Large, equivalent major restoration	Maximal, equivalent to rebuilding.
Capital Cost	Nominal <$1,000	Low $1,000-$10,000	Moderate $10,000-$100,000	High >$100,000
Waste Treatment Cost	Landfill in place or burn in place	Uncontrolled landfill or Incinerate on site	Hazardous landfill Special Incineration	Permanent Storage

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TABLE 7. CONCEPTS EVALUATED IN PHASE I

Thermal	Abrasive
Hot Gases	Vacu-Blast
Radiant (Infrared) Heating	Hydroblasting
Flaming	Acid Etch/Neutralization
Microwaves	Sandblasting
Burning to Ground	Scarifier
Flashblasting	Demolition
Electrical Resistance Contact Heating	Crygenics
Solvent Soak/Controlled Burning	Ultrasonic Extraction
CO_2 Laser	Electropolishing
Hot Plasma	Drill and Spall

Extraction	Chemical
Steam Cleaning - External	Radical Initiated Decomposition
Surfactants	Base Initiated Decomposition
RadKleen	Reduction with Sodium Borohydride
Strippable Coating	Sulfur Based Reduction
Vapor Phase Solvent Extraction	Reductive Cleavage
Steam Cleaning - Manual	Microbial Degradation
Solvent Circulation	DS_2
Supercritical Fluids	Gamma Radiation
	Reactive Amines
	Ultraviolet Light/Hydrogen Peroxide
	Molten Reactant Systems
	Active Metals and Acids
	Nucleophilic Displacement
	Ozone
	Ascorbate
	Solid-State Hydrogen
	Inerting by Solubilization

Inerting	White Phosphorus
Inerting by Solubilization	Water-Entrained Air
Inerting by Denitration	Hypohalogenites
Formation of Water Soluble Derivatives	Aqueous Cupric Sulphate
Desensitization by Water	Mineral Oil Emulsion
Desensitization by Steaming	
Desensitization with Reductants	
Desensitization with Stabilizer Coatings	
Decomposition with Reactive Amines	

There were several concepts which did not score well in the
evaluation scheme, but showed potential for a specific application. These
concepts may be suggested for Phase II study if their specific application
is shown to exist in structures in need of decontamination. Brief de-
scriptions of these specific concepts can be found in Section 7.5.

7.0 DECONTAMINATION OF EXPLOSIVES

7.1 THERMAL DECOMPOSITION OF EXPLOSIVES

7.1.1 Introduction

The state-of-the-art method for restoration of buildings con-
taminated with explosive residues is by flaming. The flaming technique
developed by Rockwell Inc. was employed to decontaminate several buildings
at the Frankford Arsenal (Lillie, 1981).

During the course of this study, low temperature (under 600 F)
thermal decomposition data for the explosives of interest were located.
The data revealed that complete decomposition of the explosives could be
accomplished at mild temperatures. In most cases, inocuous gaseous pro-
ducts were formed. Thus, several alternatives were investigated to supply
heat as a means of in situ thermal decontamination of a building.

7.1.2 Thermal Decomposition Chemistry and Kinetics

7.1.2.1 RDX

RDX decomposes either by fragmentation of the ring by C-N
cleavage, by removal of nitro groups from the ring, or by elimination of
HONO from the ring (Farber, 1979; Schroeder, 1979; Rauch, 1969). The
following are illustrations of the three reported mechanisms:

C-N Cleavage

NO₂ Removal

$$:NCH_2 + NO_2{-}_N{\diagup}^{CH_2} \longrightarrow NO_x + H_2O + N_2 + CO+...$$

HONO Elimination
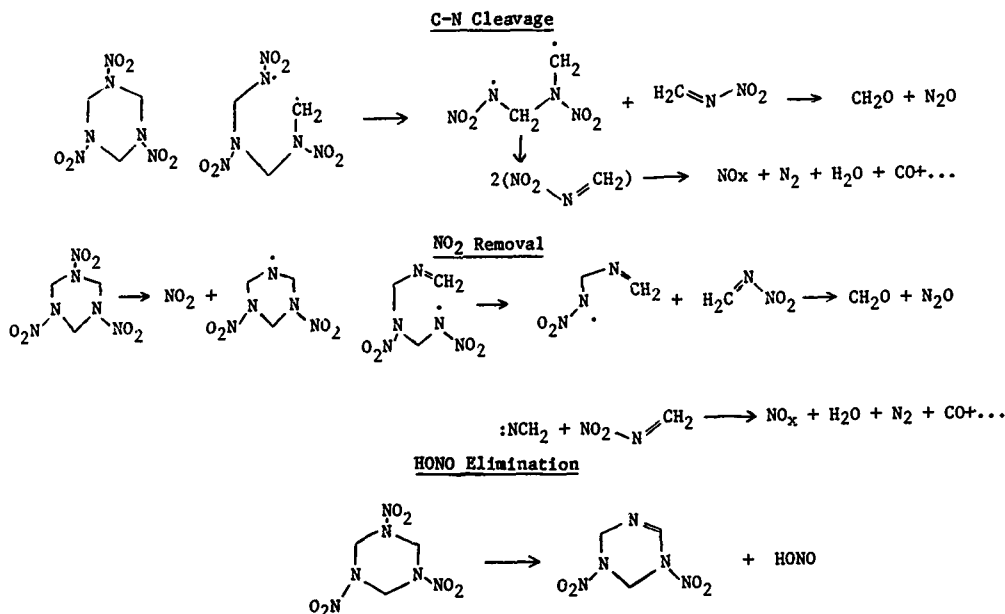
Table 8 lists reported RDX thermal decomposition products as well as the product distribution. The thermal decomposition of RDX is autocatalyzed by its decomposition products. Autocatalysis is demonstrated by a slow-rate (induction) period during the initial stages of thermal decomposition. As the products increase in concentration, the rate of reaction increases (Batten, 1969). Among the products listed in Table 8, N_2O, HCN, CH_2O and N-hydroxy-N-methylformamide, have been reported to catalyze the reaction whereas NO_2 and H_2O have been reported to inhibit the reaction.

Other materials have been shown to catalyze the reaction including several types of waxes (Joyner, 1970), UV light (Batten, 1972),

TABLE 3. RDX THERMAL DECOMPOSITION PRODUCTS

Decomposition Products	Comments	Product Distribution* (Moles/Moles RDX Decomposed)	Selected References
Gaseous			
NO	Primary decomposition product (Schroeder, to be published)	0.23-1.30	1,2,3
N_2O	Catalyzes decomposition reaction (Kolb, 1981; Batten, 1971; Batten, 1970)	0.76-1.40	4,5,6
NO_2	Minor product (Coshgarian, 1976) Reacts as it is formed (Schroeder, 1981) Inhibits decomposition reaction (Batten, 1970; Batten, 1971)	Present	7,8,9
N_2		0.65-1.26	6,9,10
NH_3	Forms below melting point (Farber, 1979; Cosgrove, 1974)	0.34-0.83	1,2
HCN	Minor product (Batten, 1970) Low yields at low temperature (Schroeder, 1981) Yield increases with increasing temperature (Schroeder, 1981) Reacts further during slow thermal decomposition (Schroeder, 1981)	0.03-0.23	3,6,9
H_2O	Catalyzes decomposition reaction (Kolb, 1981) Inhibits decomposition reaction (Batten, 1971; Batten, 1970; Batten, 1971)	Present-0.97	3,8,9
H_2		0.06-0.09	11,12,14
CO	Secondary decomposition product (Schroeder, to be published)	0.16-0.76	2,9,10
CO_2	Secondary decomposition product (Schroeder, to be published)	0.30-0.89	1,4,8
CH_2O	(Formaldehyde) Catalyzes decomposition reaction (Batten, 1971; Batten, 1970; Batten, 1971)	0.97-1.20	2,7,12
CH_2O_2	(Formic Acid) Forms below melting point (Farber, 1979; Cosgrove, 1974)	0.37-0.93	1,2

TABLE 8. (Continued)

Decomposition Products	Comments	Product Distribution* (Moles/Moles RDX Decomposed)	Selected References
Solid			
HCON(OH)Me	N-Hydroxy - N-Methylformamide Catalyzer Decomposition Reaction (Batten, 1971; Batten, 1970; Batten, 1971)	Present	12,13

*Schroeder, 1981.

1 = Farber, 1979
2 = Cosgrove, 1974
3 = Batten, 1970
4 = Perrault, 1979
5 = Schroeder, 1980
6 = Schroeder, 1981
7 = Kolb, 1981
8 = Goshgarian, 1976
9 = Rauch, 1969
10 = Urbanski, 1964
11 = Robertson, 1949
12 = Schroeder, to be published
13 = Kimura, 1980
14 = Andreyev, 1969

gamma radiation (Avrami, 1976), asphaltic and alkyd paints (Joyner, 1970, Joyner 1969) nuclear radiation (Batten, 1972), $CuSO_4$ (Batten, 1971), carbazole (Batten, 1971) and methanol (Batten, 1971). Plasticizers (Perrault, 1979) have also been reported to inhibit the reaction.

Arrhenius expressions for the temperature effect on the rate constant have been cited for thermal decomposition in the solid phase (Miles, 1972; Hall, 1970; Goshgarian, 1976; Schroeder -- to be published) and liquid phase (Schroeder, 1980; Urbanski, 1964; Rauch, 1969). The following are expressions for the rate constant (k) (Schroeder, 1980):

Solid Phase RDX

k (sec^{-1}) = 4.0 x 10^{18} exp (-51,000/RT)

temperature range = 150-197 C

Liquid Phase RDX

k (sec^{-1}) = 4.7 x 10^{18} exp (-47,800/RT)

temperature range = 207-299 C

where T = Temperature ($^{\circ}K$)

R = Gas constant = 1.987 cal/gmmole $^{\circ}K$

The above expressions include autocatalytic and gas phase decomposition effects.

A number of kinetic studies have been performed on the thermal decomposition of RDX. The rate of thermal decomposition of RDX has been shown to follow first order kinetics (Schroeder -- to be published; Urbanski, 1964; Robertson, 1949) although complex kinetics may be observed under some conditions (Schroeder, 1979; Schroeder -- to be published). The literature indicates that RDX melts (mp = 204 C) before rapid and extensive decomposition occurs (Goshgarian, 1976; Schroeder, 1979; Kishore, 1978). However, Cosgrove (1974) showed that at 195 C, 83 percent of the RDX decomposed in less than 4 hours. Kreyenhagen (1962) showed that the rate of gas evolution substantially increased between 185 and 190 C.

The following first order rate equation can be used to describe the kinetics:

$$\ln \left(\frac{C}{Co}\right) = -kt$$

where C $=$ Concentration of RDX at time t (gmmole/cm3)

Co $=$ Initial concentration of RDX (gmmole/cm3)

k $=$ Arrhenius expression (sec^{-1})

t $=$ time (sec)

A plot of the time required for 99 percent decomposition of RDX versus temperature is given in Section 7.1.3.

There is an extensive body of literature pertaining to the thermal decomposition of RDX. Product distributions and reaction kinetics have been addressed in sufficient detail.

7.1.2.2 HMX

The mechanism of the thermal decomposition of HMX is similar to that of RDX (Kishore, 1978; Schroeder, 1979). HMX decomposition occurs either by cleavage of N-N bonds followed by reaction of NO_2 with ring fragment radicals* (Kolb, 1981; Kimura, 1980; Medvedev, 1977), by elimination of HONO** (Kolb, 1981; Farber, 1979; Schroeder, 1979; Schroeder, 1980), or by breakage of C-N bonds rather than weaker N-N bonds (Kolb, 1981; Schroeder, 1979). The NO_2 removal reaction scheme is illustrated below:

---
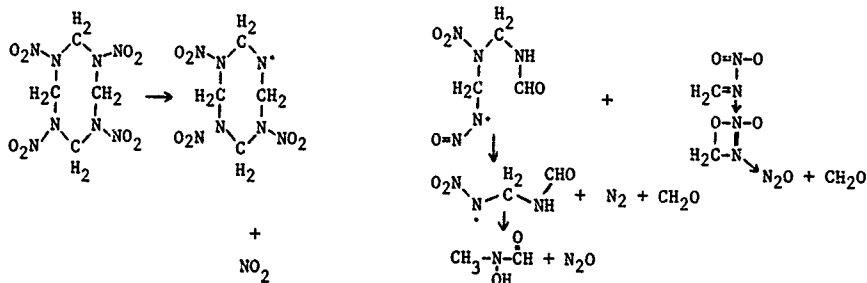
* Predominant mechanism above 300C.

** Predominant mechanism below 300C.

TABLE 9. HMX THERMAL DECOMPOSITION PRODUCTS

Decomposition Products	Comments	Product Distribution* (Moles/Moles HMX Decomposed)	Selected References
Gaseous			
NO	Primary decomposition product (Schroeder, to be published)	0.24-2.40	1,2,3,7
N_2O	Predominant product (Kolb, 1981)	1.51-2.57	1,2,4,7
NO_2	Formed in initial stages of reaction (Goshgasign, 1976) Observed at high temperatures (Goshgasian, 1976)	-	1,5,8
N_2	Reacts quickly with formaldehyde (Kolb, 1981)	0.19-1.16	1,2,3,7
HCN	Decreases with increasing temperature (Kolb, 1981) Increases with increasing temperature (Schroeder, 1981)	0.02-0.48	1,2,4
H_2O	--	Present	1,2,5
H_2	--	Present	1,2
CO	--	0.19-0.57	1,2,3,7
CO_2	--	0.16-0.64	1,2,5,7
CH_2O	Predominant product (Kolb, 1981) Catalyzes decomposition reaction (Kimura, 1980)	0.47-2.71	4,5,6
Solid			
HCON(OH)Me	(N-Hydroxy-N-Methylformamide) Major product for liquid phase decomposition (Kolb, 1981) Catalyzes decomposition reaction (Kimura, 1980)		4,6

*Schroeder, 1981.

1 = Schroeder, 1981
2 = Schroeder, to be published
3 = Robertson, 1949
4 = Kolb, 1981
5 = Goshgarian, 1976
6 = Kimura, 1980
7 = Andreyev, 1969
8 = Beyer, 1979

Table 9 gives reported HMX thermal decomposition products as well as the product distribution. The products for thermal decomposition of HMX are identical to those for RDX.

Because of the similar chemical structures of RDX and HMX, the same catalysts (and inhibitors) will similarily influence the thermal decomposition rate of both RDX and HMX. For example, formaldehyde and N-hydroxy-N-methylformamide enhance the decomposition rate of both RDX and HMX. This is important because military grade HMX contains up to 10 percent RDX (Kreyenhagen, 1962). Since the decomposition of PDX results in the formation of species which catalyze the decomposition of HMX, military grade HMX may decompose quicker and at a lower temperature than pure HMX (Kreyenhagen, 1962).

Arrhenius expressions for the temperature effect on the rate constant have been cited for thermal decomposition of HMX in the solid phase (Schroeder, 1980; Medvedev, 1977) and in the liquid phase (Schroeder, 1980; Schroeder -- to be published; Robertson, 1949). Following is an expression for the rate constant which is applicable to both solid and liquid phase thermal decomposition of HMX:

$$k \ (sec^{-1}) = 8.9 \times 10^{19} \exp (-53,100/RT)$$

As in the case of RDX, HMX follows first order kinetic behavior for the rate of thermal decomposition (Sinclair, 1971) and both exhibit exothermic and autocatalytic behavior upon heating. However, HMX is considerably more thermally stable than RDX (Kolb, 1981) so higher temperatures are required to cause decomposition of pure HMX. Pure HMX melts (mp = 280 C) before rapid and extensive decomposition occurs (Goshgarian, 1976; Andreyev, 1969; Kishore, 1978) although the rate of decomposition begins to increase at about 250 C. Several papers cited complete decomposition of HMX at temperatures at or below the melting point (Kimura, 1980; Kishore, 1978; Maycock, 1969).

An equation similar to the one given in 7.1.2.1 (with a different Arrhenius expression) was used to plot the time required for 99 per-

cent decomposition of HMX versus temperature. The plot is given in Sec-
tion 7.1.3.

As in the case of RDX, the thermal decomposition of HMX is well
documented.

7.1.2.3 TNT

The TNT thermal decomposition reaction has been described as a
three stage process (Pasman, 1969): 1) a chemical induction period where
there is little reaction, 2) an auto acceleration period where the decom-
position rate increases as a result of autocatalysis and 3) a decreasing
rate period caused by consumption of the reacting compounds.

There are conflicting reports as to the actual mechanism of de-
composition. Davis (1981) reported that TNT decomposes by removal of the
nitro groups as a result of radical formation. Dacons (1970), Maksimov
(1974), and Rogers (1967) reported the following decomposition reaction
scheme involving successive oxidation of the TNT molecule:
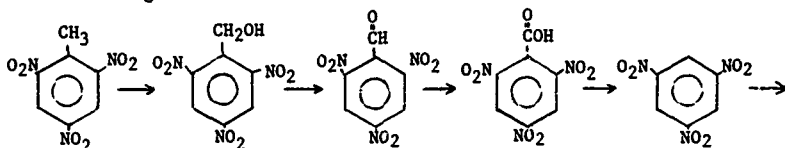
The rate controlling step in the above scheme is the cleavage of the C-H
bond (Shackelford, 1977).

Unlike HMX and RDX, TNT generates a relatively small quantity of
gaseous decomposition products during the early decomposition stages
(Roginskii, 1964; Joyner, 1970; Dacons, 1970; Rogers, 1967). The inter-
mediate products, shown in Table 10 undergo a secondary decomposition to
yield gaseous products (Joyner, 1970). For slow heating rates at temper-
atures below 200 C, 4,6-dinitroanthranil, 2,4,6-trinitrobenzaldehyde, and
"explosive coke" are the primary products (Dacons, 1970). The "explosive
coke" is a polymeric species containing some aromatic nitro groups and is

TABLE 10. TNT THERMAL DECOMPOSITION PRODUCTS

Decomposition Products	Comments	Selected References
Intermediates		
4,6-Dinitroanthranil 	Major product (Dacons, 1970) Strong decomposition catalyst (Maksimov, 1974) Decomposes much more rapidly than TNT (Kaye, 1980)	1,2,3
2,4,6-Trinitrobenzaldehyde 	Major product (Dacons, 1970) Decomposition catalyst (Kaye, 1980) Not detected (Rogers, 1967)	1,3,4
2,4,6-Trinitrobenzylalcohol 	Minor product (Dacons, 1970)	2,3,4
2,4,6-Trinitrobenzoic acid 		2,3

TABLE 10. (Continued)

Decomposition Products	Comments	Selected References
O_2N—NO_2 (with NO_2)	Not detected (Dacons, 1970) Major product (Rogers, 1967) More forms at higher heating rates (Rogers, 1967)	2,3,4
1,3,5-Trinitrobenzene O_2N—R O R—NO_2 R—N = N—NO_2 O_2N R=H, CH_3	Minor product (Dacons, 1970)	4,5
Gaseous Products NO, N_2O, N_2, CO, CO_2, H_2O, C_2H_2	Total of one mole of gas produced per mole of TNT decomposed (Guidry, 1978). NO is predominant gaseous product (Raginskii, 1964) 10 percent of TNT decomposes to gaseous products (Kreyenhagen, 1962)	5,6,7
$C_6H_3N_2O_{3.75}$	Explosive coke [melting point > 300 C (Dacons, 1970)] Strong decomposition catalyst (Kaye, 1980; Dacons, 1970) Major product (Dacons, 1970) Toluene soluble (Guidry, 1978)	1,4,8,9

1 = Kaye, 1900
2 = Rogers, 1967
3 = Shackelford, 1977
4 = Dacons, 1970
5 = Cook, 1956
6 = Robertson, 1949
7 = Sapranovich, 1973
8 = Roginskii, 1964
9 = Guidry, 1978

reasonably energetic (Dacons, 1970). For high heating rates at higher temperatures (230 C), 1,3,5-trinitrobenzene (TNB) is the major product (Rogers, 1967). TNB is thermally stable at temperatures as high as 280-300 C; however, it may also undergo secondary thermal decomposition to yield gaseous products although at a much slower rate than for TNT.

As in the case of most other explosives, the products from thermal decomposition of TNT catalyze the reaction (Andreyev, 1969; Roginskii, 1964; Kreyenhagen, 1962). Several other reports indicate that other catalysts enhance the thermal decomposition of TNT including:

- HMX decomposition products (Wilby, 1963)
- RDX decomposition products (Wilby, 1963)
- Carbon or other easily oxidized material (Deason, 1959)
- UV light (Robertson, 1948)
- KCL, KNO_3 (Pasman, 1969)
- Ammonia gas (Robertson. 1948)
- MnO_2, Fe_2O_3, $KMnO_4$, Cobalt compounds (Robertson, 1948)
- Benzophenone, diphenylamine, various waxes (Robertson, 1948)
- Hydroquinone, benzoic acid (Shackelford, 1977)
- Prior heating (Ellison, 1980)
- Asphalts, 405 wax, 450 wax, alkyd paints (Joyner, 1970)
- Stainless steel welding impurities (Kreyenhagen, 1962)

Zeman (1979) found a reduced thermal stability of TNT when heated in glass containers which was a caused by an interaction of TNT with the alkaline components of the glass. Alkaline building materials (e.g. concrete) may show a similar catalytic effect on the thermolysis of TNT.

Several Arrhenius expressions for the thermal decomposition rate constant have been reported (Zeman, 1979; Cook, 1956; Robertson, 1948) with the equations and values for the rate constants at several temperatures shown in Table 11. The Arrhenius equation reported in Robertson's

TABLE 11. TNT THERMAL DECOMPOSITION ARRHENIUS EXPRESSIONS

Arrhenius Expression	Reference	k (sec^{-1})		
		200 C	250 C	300 C
k (sec^{-1}) = 2.0 x 10^9 exp (-34,520/RT)	Zeman, 1979	2×10^{-7}	8×10^{-6}	1×10^{-5}
k (sec^{-1}) = 9.5 x 10^{12} exp (-43,400/RT)	Cook, 1956	2×10^{-8}	1×10^{-6}	5×10^{-5}
k (sec^{-1}) = 2.5 x 10^{11} exp (-34,400/RT)	Robertson, 1948	4×10^{-5}	1×10^{-3}	2×10^{-2}
k (sec^{-1}) = 7.9 x 10^8 exp (-26,600/RT)	Ellison, 1980	4×10^{-4}	6×10^{-3}	6×10^{-2}
k (sec^{-1}) = 7.9 x 10^9 exp (-29,400/RT)	Beckmann, 1976	2×10^{-4}	4×10^{-3}	5×10^{-2}

work (1948) may be preferred for use in "real world" conditions because it incorporates effects such as autocatalysis and the exothermicity of the reaction into the equation. In contrast, the experiments detailed in Cook's paper (1956) focuses on the determination of the theoretical (uncatalyzed, isothermal) decomposition of TNT. The value for k at 200 C for the expression given in Robertson (1948) also corresponds closely with the k calculated from data given by Joyner (1970). Thus, the expression from Robertson (1948) will be employed in the kinetic equation describing TNT thermal decomposition.

TNT has been shown to exhibit a storage life in excess of 20 years at room temperature and over 2 years at its melting point (81 C) (Kaye, 1980). The stability of TNT at elevated temperatures has been reported in numerous studies including (Kayser, 1974; Urbanski, 1964; Robertson, 1948). Urbanski (1964) cited a temperature of 160 C where the thermal decomposition of TNT begins. A rapid reaction rate was observed at temperatures above 200 C (Dacons, 1970; Roginskii, 1964). Complete decomposition of TNT was reported after heating TNT at 300 C for 75 minutes leaving a charred residue (Kayser, 1974); however, Guidry (1978) demonstrated that nearly complete decomposition occurred when TNT was heated at 285 C for about 10 minutes. Thus, in contrast to most other explosives, TNT requires temperatures well above its melting point to cause marked decomposition. Also, decomposition is primarily a liquid phase phenomena with TNT vapor being stable at a temperature of 300 C (Cook, 1956; Guidry, 1978). Further, Maksimov (1971) estimated that the decomposition rate for liquid TNT is at least an order of magnitude greter than for vapor TNT.

The decomposition reaction has been shown to follow first order kinetics (Shackelford, 1977; Beckmann, 1976; Guidry, 1978) following a slow rate induction period lasting 5-10 minutes (Ellison, 1980). The first order kinetic equation, similar to the one given in Section 7.1.2.1, employs the rate constant from Robertson (1948). A plot of the time required for 99 percent decomposition of TNT versus temperature is given in Section 7.1.3.

It is important to note that the reaction rate may be increased (a decrease in reaction time or an increase in rate at lower temperatures) by adding a catalyst such as those previously listed. For example, a half life of pure TNT at 190 C was given as 43,200 seconds while for TNT with 405 wax added the half life was only 732 seconds (Joyner, 1970).

The results reported on the thermal decomposition of TNT are conflicting in many cases.

7.1.2.4 DNT

The mechanism of thermal decomposition of DNT is similar to that of TNT (Maksimov, 1971). In TNT; 2,4-DNT and 2,6-DNT, the nitro groups are in an ortho position relative to the methyl group. For this positioning, the most energetically favorable thermal decomposition mechanism in the vapor phase is a rapid intermolecular oxidation of the CH_3 group with retention of the C-N bond (Maksimov, 1972; McMillen, 1981). However, in a melt (i.e. liquid phase) abstraction of a NO_2 group through C-N bond cleavage may be the predominant mechanism (Maksimov, 1971). The thermal decomposition of 2,4-DNT and 2,6-DNT results in the formation of about 3 to 3.5 moles of gas per mole of DNT decomposed (Maksimov, 1972). The gas is in part composed of NO, NO_2 and H_2O (Maksimov, 1971). In addition to gaseous products a brown solid deposit forms in thermolysis of DNT (Maksimov, 1972) which is similar to that formed in thermolysis of TNT.

As in TNT, the DNT thermolysis reaction is autocatalytic (Maksimov, 1972). The influence of a catalyst on the decomposition rate was described in (Small, 1973) where the presence of 2.5 percent Na_2CO_3 decreased the decomposition temperature of DNT from 260-290 C (neat DNT) to 197-242 C. Because of the similar chemical structure, catalysts which increase the rate of thermal decomposition of TNT are expected to increase the rate of DNT thermolysis.

The temperature dependence on the thermal decomposition rate constant was reported by Maksimov (1972), McMillen (1981) and Zeman (1979). The following are expressions from Zeman (1979):

2,4 DNT
$$k \ (sec^{-1}) = 10^9 \ exp \ (-33,350/RT)$$

2,6 DNT
$$k \ (sec^{-1}) = 2 \times 10^{14} \ exp \ (-47,530/RT)$$

Several investigations of the rate of thermal decomposition of 2,4-DNT and 2,6-DNT have been performed (Zeman, 1979; Maksimov, 1972; Small, 1973 and McMillen, 1981). Maksimov (1972) determined that the 2,6 isomer has the fastest decomposition rate of all of the DNT isomers. Maksimov (1971) also showed that the decomposition rate in the liquid DNT phase was greater than the rate in the vapor phase because of intermolecular interaction in the liquid phase which facilitate the decomposition. The rate of thermal decomposition of DNT is initially slow during an induction period after which the rate accelerates. Small (1973) indicated that after an induction period of several hours at relatively low temperatures (150-200 C), the decomposition rate became significant. Since definitive kinetic data is lacking, it was assumed that the decomposition of 2,4 DNT and 2,6 DNT followed first order kinetics. Plots of the time for 99 percent decomposition of DNT versus temperature are given in Section 7.1.3.

Incomplete information is available on the kinetics and products of thermal decomposition of either 2,4 DNT or 2,6 DNT.

7.1.2.5 Tetryl

The primary step in the thermal decomposition of tetryl is reported (Kaye, 1980) as:
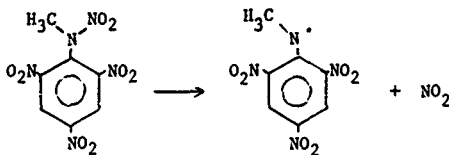
Subsequent reaction steps are unknown. Dubovitskii (1961) indicated that the primary reaction step yields picric acid as follows:
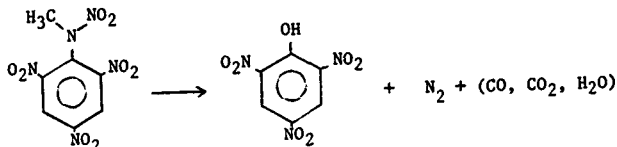
The products of the thermal decomposition of tetryl are given in Table 12. It is important to note that although picric acid is a major decomposition product it will decompose to volatile products upon further heating (Hara, 1975).

The thermal decomposition of tetryl is catalyzed by the intermediate product picric acid. Other catalysts or inhibitors have not been reported.

Several studies determined the Arrhenius expression for tetryl decomposition (Robertson, 1948; Dubovitskii, 1961; Cook, 1956; Kaye, 1980). Two distinct experimental methods used to obtain kinetic data (heat evolution and gas evolution) resulted in quite different expressions (Urbanski, 1964). The method employing measurement of gas evolution used by Robertson (1948) and Dubovitskii (1961) is probably the more realistic because it incorporates autocatalytic effects. The following is the Arrhenius expression from Robertson (1948):

$$k \ (sec^{-1}) = 2.5 \times 10^{15} \exp (-38,400/RT)$$

It has been reported (Urbanski, 1964) that tetryl has a storage life at room temperature in excess of 20 years. However, as the melting point of tetryl (130 C) is reached, the decomposition rate increases sharply (Urbanski, 1964; Farmer, 1920). Dubovitskii (1961) reports that tetryl is completely decomposed at 150 C in about 450 minutes and at 160 C in about 150 minutes. For the plots of time for 99 percent decomposition of tetryl versus temperature (given in Section 7.1.3), it was assumed that the reaction followed first order kinetics.

The state-of-the-art for tetryl thermal decomposition is quite well developed.

TABLE 12. TETRYL THERMAL DECOMPOSITION PRODUCTS
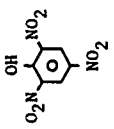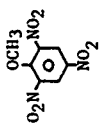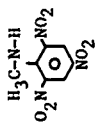
Decomposition Products	Comments	Selected References
Solid		
Picric Acid structure (OH, NO_2, O_2N, NO_2) Picric Acid	Major decomposition product (Dubovitskii, 1961; Kaye, 1980) Amount increases with reaction time (Kaye, 1980) Catalyzes decomposition reaction (Kaye, 1980; Dubovitskii, 1961) Begins to decompose at 160 C evolving NO_2 (Hara, 1975)	1,2,3
Trinitroanisole structure (OCH_3, NO_2, O_2N, NO_2) 2,4,6-Trinitroanisole	Retards reaction rate (Kaye, 1980) Major product at initial stages of decomposition (Kaye, 1980) Disappears after prolonged heating to form picric acid (Kaye, 1980)	2,3,6
Trinitroaniline structure (H_3C-N-H, NO_2, O_2N, NO_2) N-Methyl-2,4,6-trinitroaniline	--	2,3

TABLE 12. (Continued)

Decomposition Products	Comments	Selected References
Gaseous		
CO_2	About 0.5 moles form per mole tetryl decomposed (Kaye, 1980)	3,4,5
CO	About 0.2 moles form per mole tetryl decomposed (Kaye, 1980)	1,3,5
NO	About 0.15 moles form per mole tetryl decomposed (Kaye, 1980)	2,3,4
NO_2	Less than 0.03 moles form per mole tetryl decomposed (Kaye, 1980)	2,3
N_2	Major product (Urbanski, 1964; Dubovitskii, 1961)	1,3,4
N_2O	About 1 mole forms per mole of tetryl decomposed (Urbanski, 1964)	4
	--	

1 = Urbanski, 1964
2 = Dubovitskii, 1961
3 = Kaye, 1980
4 = Robertson, 1948
5 = Farmer, 1920
6 = Price, 1976

7.1.2.6 Nitrocellulose

Nitrocellulose is a high molecular weight compound which, because of its inability to melt or vaporize, thermally decomposes in the solid state (Andreyev, 1969). There are three modes in which nitrocellulose (NC) is thermally degraded:

> 1) Hydrolysis of ester ($-ONO_2$) groups which accounts for 1/3 to 1/2 of the decomposition reaction (Leider, 1981; Kageyama, 1973; Wolfrom, 1956),
>
> 2) Hydrolysis of linkages between glucose units (Urbanski, 1964),
>
> 3) Intermolecular oxidation (Urbanski, 1964).

The degradation process results in depolymerization of the NC with subsequent formation of volatile and gaseous species.

Table 13 lists the products formed on thermal decomposition of NC at elevated temperatures (300 C). Gaseous products predominate as illustrated in Table 13. At lower temperatures (175-250 C), NC tends to decompose to a nonvolatile residue (Ettre, 1963). However, Urbanski (1964) has shown that NC decomposes at 150 C by the following equation:

$$C_{24}H_{29}O_9(NO_3)_{11} \longrightarrow 6.27\ CO_2 + 3.58\ CO + 5.37\ NO + 2.70\ N_2 + 8.0\ H_2O$$
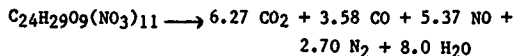
The decomposition reaction is autocatalytic since the rate of reaction was shown to increase when the gaseous deomposition products were allowed to accumulate near the surace of the decomposing NC (Andreyev, 1967). Experiments have shown that an oxygen atmosphere enhances the decomposition rate (Andreyev, 1967), whereas an inert atmosphere inhibits the rate (Seborg, 1961). Lead has also ben shown to catalyze the decomposition of NC (Baumann, 1965).

TABLE 13. NITROCELLULOSE THERMAL DECOMPOSITION PRODUCTS

Decomposition Products	Percent of Original NC After Treatment at 300 C(a)	Selected References	
Gaseous			
NO	(b)	1,2,3	Formed by reduction of NO_2 (Volltrauer, 1981)
N_2O	(b)	4,5,6	Rapidly reduced by NC to NO (Volltrauer, 1981)
NO_2	(b)	4,6,7	Primary decomposition product (Volltrauer, 1981) / Catalyzes decomposition reaction (Andreyev, 1967) / Inhibits reaction rate (Seborg, 1961)
N_2	1.7	3,4,6	
HCN	–	3,5,8	
H_2O	12.0	1,4,6	Water vapor increases reaction rate (Lurye, 1969; Andreyev, 1967)
CO	37.5	2,3,5	
CO_2	(a)	1,4,6	
CH_2O	–	3,5,6	
CH_4	–	3,4	
C_2H_4	1.5	4	
H_2	–	3	
Volatile			
Acetone		8	
Acetaldehyde	2.0	4,8	
Acrolein	$CH_2=CHCH(O)$	8	
Methyl Acetate	0.3	4,8	
Ethyl Acetate	–	4,8	
Methanol		8	
Ethanol	2.0	8	
Glyoxol	2.0 $HC(O)-CH(O)$	8	
Formic Acid	–	3,5	
α-Hydroxy Nitrile	–	3,5	
	–	3,5	

TABLE 13. (Continued)

Decomposition Products	Percent of Original NC After Treatment at 300 C[a]	Selected References
Non-Volatile Residual Solids	6.5	4

(a) Ettre (1963)
(b) $CO_2 + NO_x = 20.5$ percent.

1 = Lurye, 1969
2 = Kageyama, 1973
3 = Wolform, 1956
4 = Ettre, 1963
5 = Wolfrom, 1958
6 = Gelernter, 1956
7 = Volltrauer, 1981
8 = Wolfrom, 1959

Arrhenius expressions for the rate constant have been reported (Dahn, 1980; Leider, 1981; Volltrauer, 1981; Urbanski, 1964). The following expression (Urbanski, 1964) was selected because it yields the most conservative values:

$$k \ (sec^{-1}) = 3x10^{14} \ exp \ (-37,700/RT)$$

As with most explosives, the stability of nitrocellulose at room temperature is on the order of years. Decomposition begins at about 160-170 C (Urbanski, 1964; Takehiro, 1958). At a slightly higher temperature (195 C), NC decomposes rapidly (Kageyama, 1973), indicating its thermal instability at moderate temperatures.

Several investigations have been made of the kinetics of NC thermal decomposition (Leider, 1981; Volltrauer, 1981; Andreyev, 1969; Seborg, 1961). The decomposition has been shown to follow second order kinetics (Leider, 1981) by:

$$2 \ RONO_2 \ \longrightarrow \ Products$$

The integrated kinetic equation is then:

$$\frac{1}{C_0} \left[\frac{C_0 - C}{C} \right] = kt$$

where $C_0 = 2.31$ (mean ester number of nitrocellulose)

C = concentration at time t ($gmmole/cm^3$)

k = Arrhenius expression (sec^{-1})

t = time (sec)

A plot of the time versus temperature for NC thermal decomposition is given in Section 7.1.3.

The state-of-the-art of NC thermal decomposition is quite well developed. However, more information is required concerning the kinetic parameters of decomposition for the specific types of NC (i.e. 12.6% N, 13.45% and 14.14% N).

7.1.2.7 Nitroglycerin

The thermal decomposition mechanism of nitroglycerin (NG) is reported to follow several stages (Andreyev, 1963; Svetlov, 1963). Waring

(1970) gives the following as the mechanism:

$$
\begin{array}{c}
H_2CONO_2 \\
\diagdown \\
HCONO_2 \\
\diagup \\
H_2CONO_2
\end{array}
\rightleftharpoons
\begin{array}{c}
H_2CONO_2 \\
\diagdown \\
HCO\cdot \quad + NO_2 \\
\diagup \\
H_2CONO_2
\end{array}
$$

$$
\begin{array}{c}
\downarrow \\
HCO \\
| \\
H_2CONO_2 + NO_2 + CH_2O \\
| \\
HOC\cdot + CH_2O + NO_2
\end{array}
$$

$$CH_2O + NO_2 \longrightarrow HCO\cdot + HNO_2$$

$$HCO\cdot + NO_2 \longrightarrow HCOO\cdot + NO$$

$$HCO\cdot + NO_2 \longrightarrow CO + HNO_2$$

$$HCOO\cdot + NO_2 \longrightarrow CO_2 + HNO_2$$

$$2HNO_2 \longrightarrow H_2O + NO + NO_2$$
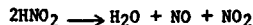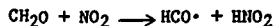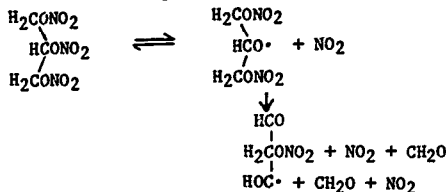
The overall reaction can be described as follows:

$$2C_3H_5(NO_3)_3 \longrightarrow H_2CO + 3CO + 2CO_2 + 6NO + 4H_2O$$
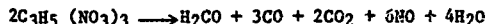
The decomposition products are listed in Table 14.

Aside from the decomposition products, other materials catalyze the reaction including H_2SO_4 and HNO_3 (Andreyev, 1958; Glazkova, 1955; Gorbunov, 1963). Water will catalyze the reaction by forming nitric acid with gaseous NO_x (Gorbunov, 1963). Diphenylamine will inhibit the reaction by combining with nitric acid to prevent the catalytic action of the acid (Glazkova, 1955). Soda and chalk will similarily inhibit the reaction (Andreyev 1969).

Several Arrhenius expressions have been reported (Svetlov, 1963; Dahn 1980; Urbanski, 1964; Serbinov, 1959; Waring, 1970). The expressions given in Waring's work (1970) for the vapor and liquid phase decomposition of NG will be used for kinetic calculations because they yield conserva- tive values of k when compared to the other equations. The expressions are as follows:

Liquid NG

$$k\ (sec^{-1}) = 1.6 \times 10^{20} \exp(-46,900/RT)$$

Vapor NG

$$k\ (sec^{-1}) = 3.2 \times 10^{15} \exp(-36,000/RT)$$

TABLE 14. NITROGLYCERIN DECOMPOSITION PRODUCTS

Decomposition Product	Comments	Quantity of Product* (percent)	Selected References
NO		38.4	1,2
NO$_2$	Catalyzes decomposition reaction (Svetlov, 1961; Urbanski, 1964)	2.2	3,4,5
	Inhibits reaction (Waring, 1970)		
	Primary decomposition product (Svetlov, 1958)		
N$_2$			5
HNO$_3$	Catalyzes decomposition reaction (Andreyev, 1958; Glazkova, 1955; Urbanski, 1964)		5
H$_2$O	Catalyzes decomposition reaction (Andreyev, 1963; Gorbunov, 1963; Urbanski, 1964)		1,2,5
CO		19.3	1,2
CO$_2$		11.5	1,2
CH$_2$O	Formaldehyde		1,2

*Waring, 1970 (remaining products which were not quantitatively analyzed include CH$_2$O, etc.).

1 = Krastins, 1957
2 = Waring, 1970
3 = Svetlov, 1950
4 = Svetlov, 1961
5 = Urbanski, 1964

NG begins to decompose at mild temperatures (about 50 C)
(Urbanski, 1964). The decomposition rate increases to the boiling point
(145 C) where the rate is rapid.

The decomposition reaction has been reported to be autocatalytic
(Andreyev, 1958; Gorbunov, 1963; Krastins, 1957) and to follow first order
kinetics (Andreyev, 1958; Waring, 1970). In the plot of the time required
for 99 percent decomposition of NG versus temperature (See Section 7.1.3)
a first order kinetic expression was used.

The state-of-the-art for thermal decomposition of NG is well
developed. However, work should be performed to determine appropriate
reaction inhibitors to prevent the occurence of an explosi^n as a result
of over-heating.

7.1.2.8 Nitroguanidine

The mechanism for the thermal decomposition of nitroguanidine
(NQ) is unknown although the two crystalline modifications of NQ (α and β)
decompose similarily (Pasman, 1973).

Volatile products of the thermal decomposition of NQ include NO_x
compounds (Pasman, 1973) and water (Popolato, 1979). A solid decomposi-
tion product, identified by Popolato (1979), has the formula
$CH_{1.13}N_{1.26}O_{0.07}$ indicating incomplete decomposition occurs when NQ
is heated in an inert atmosphere.

NO_2, a decomposition product, has been reported to catalyze
the reaction (Pasman, 1973). Other catalysts or inhibitors are unknown.

Bailey (1974) and Popolato (1979) reported the following rate
constant expression:

$$k \ (sec^{-1}) = 2.84 \times 10^7 \exp \ (-21,000/RT)$$

Several references have reported the kinetics of NQ thermal de-
composition (Pasman, 1973; Popolato, 1979; Bailey, 1974). Pasman (1973)
indicated that in open reaction vessels, thermal decomposition increases
near the melting point (232 C) where liquid NQ rapidly decomposes.

Differential thermal analysis of NQ reveals an exotherm at 250 C which may indicate decomposition (Satriana, 1968).

In the plot of the time required for 99 percent decomposition of NQ versus temperature plot, (given in Section 7.1.3) a first order rate expression was assumed.

Little information is available on the thermal decomposition of NQ.

7.1.2.9 Ammonium Nitrate

The mechanism of decomposition of ammonium nitrate (AN) has been reported by Smith (1957), Koper (1970) and Feick (1954). The initial reaction is the highly endothermic step:

$$NH_4NO_3 \rightleftharpoons HNO_3 + NH_3$$

Following this primary step, two distinct mechanisms have been suggested. The first is formation of N_2O and H_2O from an exothermic reaction involving NH_3 and catalyzed by HNO_3 (Smith, 1957; Koper, 1970; Feick, 1954). The second suggested mechanism is as follows (Rozman, 1960; Koper, 1970):

$$2HNO_3 \longrightarrow 2NO_2 + H_2O + 1/2 \; O_2$$

$$NH_3 + 2NO_2 \longrightarrow N_2 + H_2O + HNO_3$$
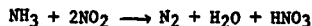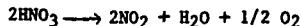
These reactions predominate at higher temperature (200 C)

The thermal decomposition products of AN are given in Table 15. The thermal decomposition of AN is reported to be autocatalytic with nitric acid being an intermediate product that behaves as an acid catalyst (Sivolodskii, 1958; Bozadzhiyev, 1975; Smith, 1957). Other compounds have been reported to enhance the thermal decomposition reaction including chloride ion or chlorine gas (Koper, 1970), polyphosphoric acid (Bozadzhiyev, 1975), graphite, Al_2O_3 or stainless steel (Flora, 1971). The addition (or presence) of one or more of these catalysts causes initiation of decomposition at a much lower temperature (100 C) than neat AN (Bozadzhiyev, 1975; Flora, 1971).

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TABLE 15. AMMONIUM NITRATE THERMAL DECOMPOSITION PRODUCTS

Decomposition Product	Comments	Selected References
N_2O	--	1,2,3
NO_2	Intermediate product (Rozman, 1960)	4,7,8
NO	Catalyzes decomposition reaction (Sivolodskii, 1958)	8
N_2	--	3,4,8
NH_3	Intermediate (Rozman, 1960; Koper, 1970; Feick, 1954)	5,6
HNO_3	Acid catalyst (Rozman, 1960; Smith, 1957; Koper, 1970)	5,6,7
H_2O	Catalyzes decomposition reaction (Sivolodskii, 1958)	2,3,4,8
O_2	--	3,4

1 = Pany, 1975
2 = Smith, 1957
3 = Koper, 1970
4 = Rozman, 1960
5 = Cawthon, 1955
6 = Feick, 1954
7 = Sivolodskii, 1958
8 = Krien, 1965

Cook (1956) reported an Arrhenius expression for the rate constant as follows:

$$k \text{ (sec}^{-1}) = 1.9 \times 10^{12} \exp(-38,300/RT)$$

Smith (1957) corrected this equation taking into account the equilibrium vapor pressure of AN to eliminate the effect on the equation of loss of AN from the test chamber by evaporation. The corrected equation is as follows:

$$k \text{ (sec}^{-1}) = 4.9 \times 10^{11} \exp(-51,000/RT)$$

As with most explosives, the initiation of rapid decomposition of AN begins at its melting point (170 C) (Kayser, 1974). The kinetics of the thermal decomposition of AN above and below the melting point have been reported by a number of investigators (e.g. Bespalov, 1968; Cawthon, 1955; Cook, 1956) with a consensus that the reaction follows first order kinetics (Bespalov, 1968; Cook, 1956; Smith, 1957). A plot of the time for 99 percent thermal decomposition of AN versus temperature, given in Section 7.1.3, assumes a first order kinetic expression. The state-of-the-art for thermal decomposition of AN is quite well developed. However, it may be preferable to investigate the use of catalysts to decrease the decomposition temperature and/or increase the reaction rate without causing AN to initiate.

7.1.2.10 Lead Azide

The mechanism of thermal decomposition of lead azide has been investigated by Todd (1962); Stammler (1960); and Stammler (1961). The decomposition of lead azide appears to occur in two distinct periods: 1) an induction period in which lead azide surface hydrolysis products (lead carbonate, basic lead azide) are decomposed, and 2) an acceleration period in which the decomposition is autocatalyzed by lead atoms formed at active centers during the initial stages of decomposition. In the acceleration period, the lead azide goes through a stepwise loss of nitrogen (Stammler, 1960) such as noted below:

$$PbN_6 \longrightarrow PbN_{3.25} \longrightarrow PbN_{2.53} \longrightarrow \text{Etc.}$$

Other intermediates with the general formula of $PbN_m(OH)_n$ also form during this period (Stammler, 1961).

The reported thermal decomposition products of lead azide are listed in Table 16. The formation of these products is dependent on the atmosphere. In an inert atmosphere lead metal and nitrogen are formed; in moist air, basic lead azides are formed; and in a CO_2 atmosphere, lead carbonate forms (Todd, 1962).

Water vapor has been reported to catalyze the decomposition reaction (Yoffe, 1951; Reitzner, 1961). Other catalysts are unknown. However, Jach (1966) has shown that pre-irradiating with gamma radiation enhances the thermal decomposition of lead azide.

The Arrhenius expression was given by Jach (1966) as follows:

$$k \ (sec^{-1}) = 10^{12} \exp (-36,300/RT)$$

Because of the two stage reaction (induction period followed by acceleration period), a complex kinetic expression is required. Young (1954) cites an expression which adequately fits the data:

$$[\alpha - \alpha(t)]^{1/3} = k \ (t - to)$$

where α = fractional conversion

$\alpha(t)$ = constant (0.0186 to 0.0156) for the induction period conversion

k = Arrhenius rate constant

t = time (min)

to = induction period time (constant = 20.8 to 31.9 min)

A plot of the time versus temperature for lead azide thermal decomposition is given in Section 7.1.3.

The state-of-the-art for thermal decomposition of lead azide is quite well developed.

TABLE 16. LEAD AZIDE THERMAL DECOMPOSITION PRODUCTS

Decomposition Products	Comments	Selected References
Pb Metal	Forms in inert atmospheres (Todd, 1962)	1,2,3
N_2	Forms in inert atmospheres (Todd, 1962; Rietzner, 1961)	1,2,3
PbO	--	2,3
PbN_x	--	2,4
Pb_3O_4	--	1,2
$PbCO_3$	Forms in CO_2 atmosphere (Todd, 1962)	1,2
$Pb(OH)_2$	Forms in moist air (Reitzner, 1961)	1,3
$PbN_6-PbO-nH_2O$	Basic lead oxide	1,3,4

1 = Todd, 1962
2 = Stammler, 1960
3 = Reitnzer, 1961
4 = Stammler, 1961

7.1.2.11 Lead Styphnate

Lead styphnate has been reported to decompose in three stages
as follows (Flanagan, 1961; Hailes, 1933):

> 1) Slow rate period where little or no gas is produced
>   (dehydration),
>
> 2) Acceleration period (to 50 percent decomposition),
>
> 3) First order reaction rate period.

The products of thermal decomposition of lead styphnate were
reported by Flanagan (1961) as follows:

> Solid Residue = 69.1% Pb, 12.2% C, 0.4% H, 6.2% N, 12.1% O
>
> Gaseous Residue = CO_2, H_2O, N_2, NO

CO_2 and N_2 are the primary decomposition products.

Water vapor has been shown to inhibit the decomposition reaction
(Flanagan, 1961) while pre-treating with γ-radiation enhances the reaction
rate (Jach, 1966).

The Arrhenius expression for the acceleration period was cal-
culated in this study from data given by Haile (1933). The expression is:

$$\ln k \; (min^{-1}) = 54.896 - \frac{29,543}{T}$$

where T = absolute temperature (K)

Several studies have been performed to determine the rate of
thermal decomposition of lead styphnate (Jach, 1966; Flanagan, 1961;
Tompkins, 1956, Hailes, 1933). Flanagan (1961) indicates that over 90
percent of the lead styphnate decomposed after heating in vacuo at 222.5 C
for 6 hours. For the plot of the time for 99 percent thermal decomposi-
tion of lead styphnate versus temperature, given in Section 7.1.3, it was
assumed that the decomposition follows first order kinetics throughout the
decomposition period.

There are only a few reports on the thermal decomposition of
lead styphnate. More studies are required to determine a kinetic equation
which describes the overall thermal decomposition process.

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7.1.3 Summary

7.1.3.1 Kinetics

A summary of the kinetic equations for the various explosives of interest is given in Table 17. Except for NC and Lead Azide, all of the explosives follow first order decomposition kinetics. Thus, specification of a value for C/C_o will allow solution of the equations to determine the time required for the specified conversion at a particular temperature. For the sake of comparison, it will be assumed that 99 percent of the explosive residue is decomposed. Then $C/C_o = 1-.99/1 = 0.01$. For NC which follows second order kinetics, an initial concentration (C_o) must be stipulated. It will be assumed that $C_o = 2.31$ is the mean nitrate ester number for fresh NC (Volltrauer, 1981). Thus, for 99% conversion, $C = 0.0231$. Lead azide follows nth order thermal decomposition kinetics as well as requiring an induction period. The following values will be assumed for lead azide:

$\alpha = 1-C/C_o = 0.99$

$\alpha(t)$ = Conversion during induction period = 0.02
(Young, 1954)

t_o = Induction period = 25 minutes

It is important to note that the actual conversion required will be dependent upon the actual concentration of explosive residues in the building materials and the lower detection limit from analytical procedures. A conversion higher than 99 percent will require a longer reaction time. For explosives that follow first order kinetics, twice the time will be required for 99.99 percent decomposition, three times the time for 99.9999 percent decomposition, etc. For NC, every 10 fold increase in conversion above 99 percent will require a 10 fold increase in reaction time. For lead azide, higher conversions than 99 percent will only require slightly more time (about 1.1 times for every 10 fold increase in conversion) because of the strong catalytic effects of the reaction.

TABLE 17. EXPLOSIVES KINETIC THERMAL DECOMPOSITION EQUATIONS

Explosive	Kinetic Equation
RDX	$\ln \frac{C}{C_o} = -[4.7 \times 10^{18} \exp (-47,800/RT)]t$
HMX	$\ln \frac{C}{C_o} = -[8.9 \times 10^{19} \exp (-53,100/RT)]t$
TNT	$\ln \frac{C}{C_o} = -[2.5 \times 10^{11} \exp (-34,400/RT)]t$
2,4 DNT	$\ln \frac{C}{C_o} = -[10^9 \exp (-33,350/RT)]t$
2,6 DNT	$\ln \frac{C}{C_o} = -[2 \times 10^{14} \exp (-47,530/RT)]t$
Tetryl	$\ln \frac{C}{C_o} = -[2.5 \times 10^{15} \exp (-38,400/RT)]t$
NC	$\frac{1}{C_o}\left[\frac{C_o-C}{C}\right] = [3 \times 10^{14} \exp (-37,700/RT)]t$
NG	$\ln \frac{C}{C_o} = -[3.2 \times 10^{15} \exp (-36,000/RT)]t$
NQ	$\ln \frac{C}{C_o} = -[284 \times 10^7 \exp (-21,000/RT)]t$
AN	$\ln \frac{C}{C_o} = -[4.9 \times 10^{11} \exp (-37,000/RT)]t$
$Pb(N_3)_2$	$[\alpha - \alpha(t)]^{1/3} = [10^{12} \exp (-36,300/RT)](t-t_o)*$
Pb Styphnate	$\ln \frac{C}{C_o} = -\left[\exp\left(54,896 - \frac{29,543}{T}\right)\right]t*$

*Time in minutes.

C = Concentration at time t
C_o = Initial concentration
R = 1,987 cal/gmmole °K
T = Absolute temperature (°K)
t = Time (sec) except where noted.

Plots of time versus temperature for thermal decomposition of the explosives of interest are given in Figures 9-11. As shown in the plots, relatively mild temperatures and times are required for 99 percent decomposition. For a temperature of 250 C most of the explosives will reach 99 percent decomposition in less than an hour. The exceptions are NH_4NO_3 and the two isomers of DNT. The kinetic data for decomposition of DNT is in question because it shows an unexpected stability of DNT at elevated temperatures. Further studies are required to confirm this data.

7.1.3.2 Toxicity of Products

Table 18 gives a summary of the products from thermal decomposition of the explosives of interest. As can be seen, most of the products are volatile species which, with adequate ventilation, pose minimal hazards to personnel. An exception would be the nitroaromatic intermediates formed when TNT is thermally decomposed. Several species may still be hazardous. Thus, further heating may be required to decompose the nitroaromatic intermediates to gaseous species.

7.1.3.3 Explosion Potential

A thermolytic technique to decompose explosive residues must consider that the exothermicity of the thermal decomposition reaction may lead to deflagration or explosive behavior. Deflagration may result if the rate of heat generated by the exothermic decomposition reaction exceeds the rate of heat dissipated from the explosive to the surroundings. A parameter used to denote the temperature where the rates of heat generation and dissipation are equal is the critical temperature of the explosive. If the critical temperature of an explosive is not surpassed, then heating an explosive should (theoretically) not result in an ignition/explosion reaction. The critical temperature of an explosive is
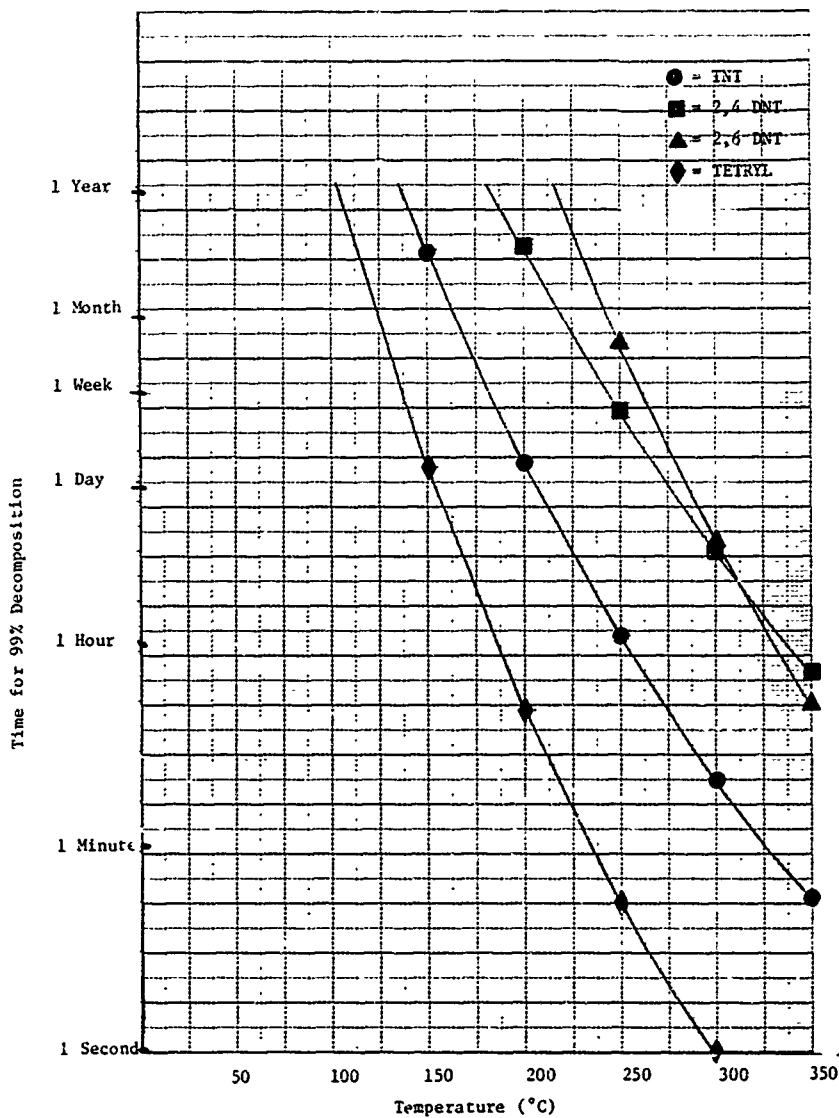
FIGURE 9.   TIME VERSUS TEMPERATURE FOR TNT, 2,4-DNT,
2,6-DNT AND TETRYL THERMAL DECOMPOSITION
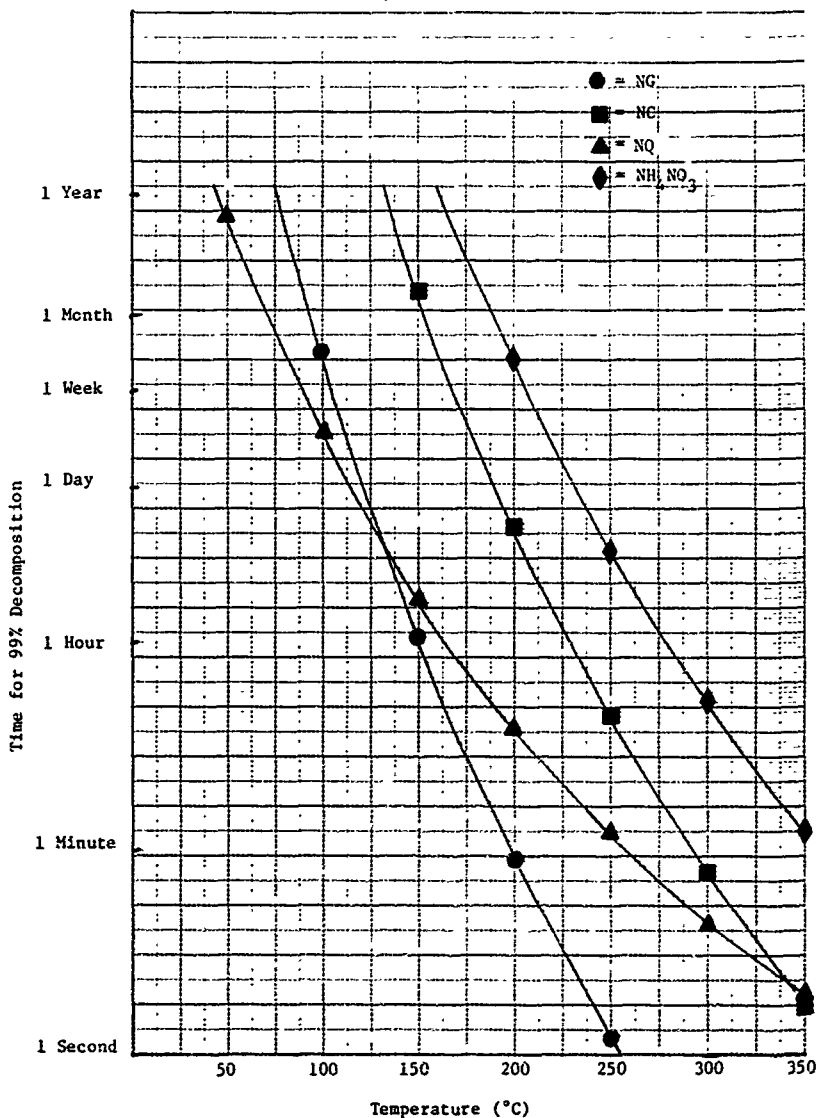
FIGURE 10. TIME VERSUS TEMPERATURE FOR NG, NC, NQ AND
NH$_4$NO$_3$ THERMAL DECOMPOSITION
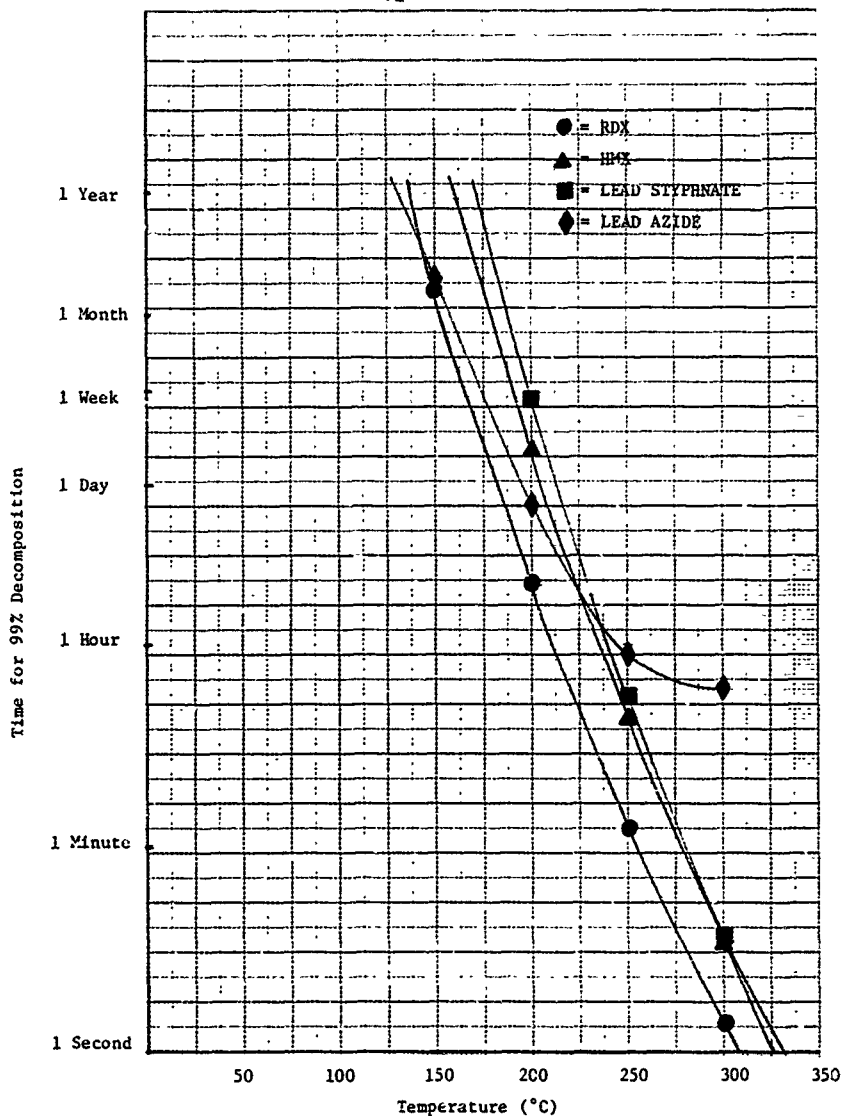
FIGURE 11. TIME VERSUS TEMPERATURE FOR RDX, HMX, LEAD
STYPHNATE AND LEAD AZIDE THERMAL DECOMPOSITION

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TABLE 18. THERMAL DECOMPOSITION OF EXPLOSIVES

Explosive	NO_x	CO, CO_2	N_2, H_2O	CH_2O	HNO_3	Lead Salts	Nitro Aromatics	Minor Species
RDX	X	X	X	X				NH_3, HCN, H_2, CH_2O_2, HCON(OH)Me
HMX	X	X	X	X				HCN, H_2, HCON(OH)Me
Tetryl	X	X	X				X*	
TNT	X	X	X				X*	C_2H_2, "Explosive" Coke $(C_6H_3N_2O_{3.75})$
2,4 DNT	X	X	X					
2,6 DNT	X	X	X					
NC	X	X	X	X				HCN, CH_4, C_2H_4, H_2, Acetates, Alcohols, Aldehydes, etc.
NG	X	X	X	X	X			
NQ	X							
NH_4NO_3	X		X		X			NH_3, O_2
Lead Azide			X			X		
Lead Styphnate	X	X	X			X		

*Intermediates.

not a fundamental property since it is a function of not only the
Arrhenius thermal decomposition parameters of the explosive but also the
physical nature of the explosive (i.e. mass, shape and concentration) and
of the surroundings (i.e. mechanism of heat transfer to and from the
explosive).

In the literature review, several references addressed the
tendency (or lack of) for neat explosives to deflagrate and/or detonate
when heated. A brief summary of these references follows.

In the case of RDX, a range of critical temperatures (199 to 270
C) were cited in the literature. Kreyenhagen (1962) observed ignition of
20 grams of military grade RDX after heating at 199 C for 20 minutes.
This amount of RDX is much less than U.S. Army (1972) reported was re-
quired to produce an explosion at 200 C (critical diameter=5.6 cm). Also,
in several studies on the thermal decomposition of RDX near its melting
point (204 C), Batten showed that heating small quantities of unconfined
RDX caused evolution of gases but no indication of ignition. Other
authors reported RDX critical temperatures between 210 and 225 C
(Popolato, 1979; Zinn, 1962; Peterson, 1976) and yet higher critical tem-
peratures of 260 to 270 C (Dahn, 1980; U.S. Army, 1971).

The critical temperature for HMX has been reported to be in the
range of 218 to 327 C. Kreyenhagen (1962) reported a violent explosion
occurred after heating 20 grams of military grade HMX (contains up to 10
percent RDX as an impurity) at 218 C for 80 minutes. A moderate critical
temperature was also reported by Zinn (1962) who showed that HMX can ex-
plode after heating at 225 C for one hour. Other investigators reported
higher critical temperatures such as 253 C (Peterson, 1976) and 327 C
(Dahn, 1980).

A wide range of ignition and explosion temperatures for pure TNT
have been reported in the literature (200 to 427 C). Kaye (1980) reported
that autoignition of TNT can occur after heating at 200 C for 38 hours.
Based on other reports, this appears to be too low of a critical temper-
ature for TNT. For example, Kreyenhagen (1962) and Roginskii (1964)

showed that TNT does not initiate when heated at 230-240 C. Further,
Kreyenhagen (1962) showed that a 20 gram sample of military grade TNT
begins to smoke rather than ignite when heated at 260 C. Most other in-
vestigators reported a critical temperature of TNT between 260 and 290 C
(Popolato, 1979; Peterson, 1976; Urbanski, 1964 and Zinn, 1962).

It has been reported that DNT will explode when maintained at a
temperature above 150 C for 2 weeks (Small, 1973).   U.S. Army (1971) in-
dicated that 2,4 DNT will rapidly decompose (not explode) after heating at
310 C for 5 seconds.

Critical temperatures for tetryl have been reported in the range
of 140 to 300 C. Merzhanov, (1981) calculated a critical temperature for
tetryl of 140 to 155 C and showed that 50 percent of the tetryl would be
decomposed before an explosion these temperatures are reached. Zinn
(1962) reported an experimental critical temperature of 200 C. Other in-
vestigators reported higher ignition/explosion temperatures such as 236 C
(Urbanski, 1964) and 257 C (U.S. Army, 1971). In contrast to these re-
ports, Henkin (1952) reported that tetryl did not explode after heating to
a temperature below 264 C.

At moderate temperatures (less than 200 C), NC decomposes with-
out ignition or explosion (Wolfrom, 1956). Henkin (1952) reported that NC
of either 12.6 percent N or 13.4 percent N content did not explode when
heated to below 170 C, however, both types of NC exploded when heated to
about 180 C. This critical temperature generally agrees with results re-
ported by U.S. Army (1971) and Dahn (1980).

It has been reported (Robertson, 1909) that unconfined NG will
not explode when heated at 90 C. If, however, the decomposition products
are allowed to accumulate, the reaction quickly accelerates until the
flash point is reached (Andreyev, 1963). Heating at higher temperatures
(215-220 C) will cause initiation of any NG present (Kayser, 1974; Henkin,
1952; Dahn, 1980).

U.S. Army (1971) reported that NQ decomposes rather than ignites
or explodes at a temperature of 275 C. In contrast, Peterson (1976) re-

ported a much lower critical temperature of between 200 and 204 C.

Ammonium nitrate has been reported to explode at a temperature as low as 225 C (Zinn, 1962). However, Kayser (1974) and Kaye (1980) reported that unconfined ammonium nitrate does not explode when heated to 300 C.

The critical temperature for lead styphnate has been reported as 280 C by Henkin (1952) and as 267 C by U.S. Army (1971). Lead azide has been reported to explode at temperatures above 282 C (Stammler, 1960) or at 320 to 340 C (Waring, 1970; Henkin, 1952). Below 250 C, lead azide decomposes without undergoing an explosion (Stammler, 1960).

Thus, the literature indicates that most of the explosives of interest have critical temperatures in the range of 200 to 300 C. For facility decontamination applications, moderate heat up rates coupled with relatively low temperature treatments would minimize the potential for an explosion by allowing the explosive to decompose slowly. Slow decomposition would allow the generated heat to be dissipated from the explosive thereby maintaining a temperature below the critical temperature. It is also important to note that the critical temperatures mentioned previously were for neat explosives. Two investigations on the thermal stability of explosives mixed with other materials showed that reducing the concentration of the explosive also reduced its tendency to ignite/explode when heated. Knight (1978) reported that wood containing up to 2 weight percent TNT did neither detonate nor explode when pyrolyzed at 650 C. Kirshenbaum (1982) determined that there is no thermal hazard when heating materials containing less than 5 percent TNT and/or RDX. These studies appear to indicate that materials containing a low concentration of explosive have sufficient heat capacity to absorb heat generated by the decomposition reaction, thereby, preventing the explosive from reaching its critical temperature before a majority of the explosive has decomposed.

When decontaminating facilities, high local concentrations of explosives may be present (i.e. pockets) which may cause a rapid increase in the localized temperature as a result of the exothermicity of the re-

action. In this case, a chemical may be applied prior to heating which would retard the reaction. An example would be the use of radical traps to intercept propagating radicals produced by the decomposition reaction.* Larkin, (1972) described the trapping of radical intermediates formed by the thermolysis of mononitrate esters. The initially formed oxygen radical was found to undergo an intramolecular gamma hydrogen abstraction to produce carbon radicals which were intercepted by bromotrichloromethane and aromatic thiols. The oxygen radicals formed during thermolysis of nitrate ester explosives (e.g. NG) may also be trapped by appropriate hydrogen donors thereby allowing thermolysis without explosion. Further work is required to identify radical traps for other explosives.

7.1.3.4 Volatility

As the temperature increases, the vapor pressure of the explosives will increase. To achieve the desired destruction efficiency, it is important that the vapor pressure of the explosives be relatively low at the working temperature to prevent migration of undecomposed explosives from the heated building material. As can be seen in Table 19, the explosives have quite low vapor pressures at elevated temperatures. Thus, volatilization of undecomposed explosives is not anticipated to have a major effect on the ultimate destruction efficiency.

7.1.3.5 Knowledge Gaps

The following knowledge gaps concerning thermal decomposition of explosives need to be addressed:

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* See Appendix III for a complete description of radical traps.

TABLE 19. VAPOR PRESSURE OF EXPLOSIVES[a]

Temperature (C)	RDX	HMX	TNT	2,4 DNT	NH$_4$NO$_3$	NG
50	<0.1 torr	<0.1 torr	<0.1 torr	<0.1 torr	<0.1 torr	<0.1 torr
100	<0.1	<0.1	0.1	0.6	<0.1	0.3
150	<0.1	<0.1	0	6	0.6	--
200	0.3	<0.1	9	38	7	(b)
250	5	<0.1	56	169	44	
300	46	<0.1	246	228	214	
350	302	0.2	(c)	--	806	

a. NC, lead styphnate, NQ and lead azide are not expected to have a vapor pressure.
    No vapor pressure data was located for 2,6-DNT and tetryl.

b. Urbanski (1964) states that NG begins to boil above 180C.

c. Boiling point = 345C.

- Behavior of explosives when heated under real world
  conditions (including explosivity and end-product
  determination)
- Reaction kinetics under real world conditions

7.1.3.6 Conclusions

Results of the literature review on the thermal decomposition of
explosives indicate that mild temperatures for relatively short periods of
time are required to decompose the explosives of interest to primarily
gaseous and volatile species.

7.1.4 Thermal-Decomposition Concepts

The following are short descriptions of the thermal decomposi-
tion concepts proposed by the project team. Detailed descriptions are
given in the Appendix III.

7.1.4.1 Flashblast

The flashblast device consists of a high intensity Xenon-
quartz strobe light which can be focused onto a contaminated surface. The
high energy light pulse produces enough heat to remove paint and rust and
to thermally decompose surface contaminants (Johnson, 1982).

Advantages
- Paint removal prior to treatment is not necessary.
- Less clean-up is required as compared with abrasive
  removal techniques.

Disadvantages
- Effective as a surface treatment only.
- Not easily adaptable to intricate surface areas.

See Section 7.5 for a discussion of the specific applicability of this concept.

7.1.4.2 Contact Heating

Heat, generated through electrical resistance coils (heating plates, tapes, etc.) applied to the building surface, would penetrate to the interior of the building material. By adjusting the temperature, the thermal decomposition of any contaminant present may be achieved, within the constraints of the building materials's thermal durability. See Appendix I for a detailed discussion of this consideration.

Advantages
o This approach may be more suitable to subsurface treatment than other thermal methods because of the possibility for greater temperature control and less extreme temperature gradients.
o The capabilities of using heat in conjunction with vacuum removal of outgassed products is also an advantage (see Appendix III).

Disadvantages
o Not easily adaptable to intricate surface areas.
o Building materials may suffer damage from thermal effects.
o Temperature gradient may promote movement of explosives deeper into the building material by thermal diffusion.

7.1.4.3 Hot Plasmas

This method is based on the use of a hot plasma (2500-20,000K) to thermally and/or chemically decompose contaminants. Thermal decomposition would result by heat transfer from the hot plasma to the contaminant. Chemical decomposition may result by reaction of ionized gases and

electrons contained in the plasma with contaminants. The mode of application could take the form of a plasma torch, which would resemble conventional flaming techniques.

Advantages

o Complete and rapid destruction of contaminants.

Disadvantages

o Potentially high utility cost.

o High temperature is likely to cause extensive damage to building materials.

o May detonate pockets of explosive residues.

7.1.4.4 Microwave Heating

Microwave heating would employ the use of microwaves to heat dielectric building materials (concrete, brick, wood, transite, etc.) to the decomposition temperature of the explosive contaminants.

Advantages

o Microwaves will penetrate concrete, wood and brick and cause heating throughout the materials, i.e. heat conduction plays only a minor role in heat transfer.

o Rapid heat-up rates can be obtained. One report (O'Kress, 1975) stated that concrete became molten after 15 minutes of irradiation with microwaves.

Disadvantages

o Sheet metal or closely spaced metal pipes will reflect the radiation without being heated.

o Building materials may be damaged by thermal effects.

7.1.4.5 Flaming

Flaming entails the use of a flame to thermally decontaminate building materials containing explosives in situ. Flaming is currently the state-of-the-art technique for installation restoration. Either hand held or remotely operated flamers may be employed as was done at Frankford Arsenal (Lillie, 1981).

Advantages
o Complete and rapid destruction of all explosive residues contacted by the flame.

Disadvantages
o Primarily a surface decontamination technique (see Section 7.1.6.3.).
o Interior decontamination of building materials may be achieved but extensive damage to the material would probably result. (See Appendix I)
o Potential for high fuel cost.
o May detonate pockets of explosive residues.

7.1.4.6 Hot Gases

The hot gases concept employs the use of heated gases such as burner exhaust gases to thermally decompose explosive residues. The circulation of hot gases in a building may allow the building to behave like an oven thereby allowing the heat to conduct throughout the building materials. Effluent gases from the building treated may be collected in an adsorber to remove NO_x and other explosive thermal decomposition products. The system can be operated until the desired time at temperature is attained to ensure explosive decomposition. Hot gases have been shown to be effective in decontamination of military vehicles exposed to chemical warfare agents (Stanford, 1981; Harstad, 1982; Magin, 1979).

<u>Advantages</u>

o Low cost burner exhaust gases may be employed to supply the
   heat.

o Inert atmosphere would minimize the fire risk.

o Low labor cost.

o Workers not directly involved in decontamination.

o All interior areas of a building (including intricate sur-
   faces) will be simultaneously heated.

<u>Disadvantages</u>

o Potential for a long decontamination time.

o Building materials may be damaged

7.1.4.7 Solvent Soak/Controlled Burning

This method consists of soaking a contaminated porous material
with a flammable solvent followed by controlled combustion of the soaked
area. Prior to ignition, the solvent would be allowed to dissolve sub-
surface contaminants. After ignition, the contaminated solvent would
diffuse to the surface to feed the flame and would, by combustion,
thermally decompose dissolved contaminants.

<u>Advantages</u>

o The method combines solvent extraction with thermal
   decomposition.

o Potentially applicable to both surface and subsurface
   contamination.

<u>Disadvantages</u>

o The solvent diffusion may be too slow to maintain surface
   combustion.

o Open fire could cause damage to surrounding areas.

o It may be difficult to control combustion which may result in
   personnel hazards.

o May detonate pockets of explosive residues.

7.1.4.8 Infrared (IR) Heating

Radiant heating employs the use of fuel or electrically powered radiant heaters to heat building materials to the decomposition temperature of the explosive. Commercial radiant heaters may be employed. Simultaneous heating of external and internal surfaces may provide more rapid heat-up rates than other thermal methods.

Advantages.
o Efficient process (at least 67% of energy supplied to heater is converted to infrared radiation) (Summer, 1965).
o No contact between heater and wall is needed. Not necessary to heat air in room.

Disadvantages.
o Heating complex surface areas in a building would be difficult because of configurations of radiant heaters.
o Building materials may be damaged by thermal stresses.

7.1.4.9 CO Laser

This method would utilize a CO_2 laser to direct an infrared laser light beam onto a contaminated building surface. Surface contaminants would be thermally decomposed directly; subsurface contaminants could be thermally decomposed by heat conduction from the irradiated surface.

Advantages.
o The laser could be centrally located in a room and operated by computer control.

Disadvantages.
o Limited to line-of-sight locations.

o A highly complex beam guidance system would be necessary.

o Building materials may suffer damage from thermal effects.

o High capital and operating costs.

o Decontamination rate may be substantially restricted by small laser beam diameter.

7.1.4.10 Burn to Ground

This method involves complete burning of a contaminated building. As the combustible material in a building burns, all contaminants would be thermally decomposed. The method has been employed for decontamination of buildings at Frankford Arsenal (Lillie, 1981) and Joliet Army Ammunition Plant (Lead Azide Line)*.

Advantages
o May be cost effective for 1940's vintage wood structures.

Disadvantages
o Building is destroyed

o Not applicable to structures composed of non-combustible materials.

o Air pollution

o Danger of fire spreading to adjacent structures.

7.1.5 Concept Evaluation

A summary of the evaluation scores for each of the thermal concepts given in Table 20. To reduce the number of concepts for the engineering analysis, a screening method to eliminate the least advantageous concepts was devised. The three step method is as follows:

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* Information obtained from Site Surveys.

TABLE 20. THERMAL DECOMPOSITION OF EXPLOSIVES CONCEPT EVALUATION

Criterion	Hot Gases	IR Heating	Flaming	Micro-Wave	Contact Heating	Burn to Ground	Flash Blast	Solvent Soak	CO$_2$ Laser	Hot Plasmas
Safety	++	++	−	+	++	−−	+	−−	+	−
Damage to Building	+	+	++	+	+	−−	++	−	+	+
Penetration Depth	+	++	−	++	++	++	−−	−	++	−
Applicability to Complex Surfaces	++	+	+	+	−	++	−−	++	−−	−−
Operating Costs	++	+	+	−	−−	+	+	−	−−	−−
Capital Costs	+	+	+	−	+	++	+	++	−−	+
Waste Treatment Costs	++	++	++	++	++	+	++	+	++	+
TOTAL	+11	+10	+5	+5	+5	+4	+3	0	0	−3

1) Any concept whose total score is less than zero is elimi
   nated because it has more disadvantages than advantages.
   This eliminates the Hot Plasma concept.

2) Any concept which scored a double minus (—) for any of the
   following criteria is eliminated: Safety, Penetration Depth
   or Applicability To Complex Surfaces. These concepts are
   eliminated because either the method may be hazardous to
   personnel, the method decontaminates surfaces only (little
   or no potential for sub-surface decontamination), or the
   method has limited application. Thus, Flashblast, Solvent
   Soak/Controlled Burning, CO_2 Laser and Burn to Ground
   concepts are eliminated.

3) Those concepts whose total score for capital and operating
   costs is less than zero are also eliminated. A negative
   number implies excessive cost for decontamination. Waste
   treatment costs are neglected because they will probably be
   a fraction of either capital or operating costs. Thus, the
   Microwave and Contact Heating concepts are eliminated.

Hot Gases, IR Heating and Flaming are the concepts that remain
for the engineering analysis.

7.1.6 Thermal Decomposition Concepts - Engineering Feasibility

In order to determine the power and equipment requirements and
the feasibility of the more promising thermal concepts, an engineering
analysis was performed using the hypothetical explosive facility described
in section 6.3 to determine the overall heat duty and operating time re-
quired. Once this analysis was completed, an economic analysis was
performed.

7.1.6.1 Engineering Feasibility of Hot Gases Concept

In order to calculate the heat duty and heating time to decontaminate the buildings specified in Section 6.3 with hot gases, several additional assumptions will be made including:

- o Hot gas is available to maintain the inside of the building at a temperature of 400 C (752 F).
- o Each building is insulated with 4 inches of insulation with thermal conductivity, k, equal to 0.05 BTU/hr ft °F.
- o 50 percent of the heat supplied to the building is lost through leakage.

The brick building will be analyzed in detail. Subsequent calculations for other buildings followed the same calculation methodology, but the results will only be summarized here.

7.1.6.1.1 Brick Building

The heat required to raise the temperature of the brick walls and ceiling to steady-state conditions is calculated as follows. The temperature gradient in the brick is illustrated below:
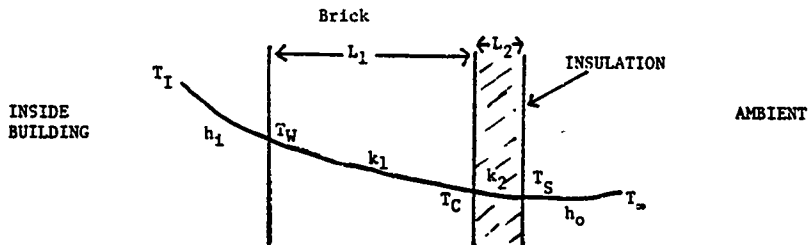
T_I = Inside atmosphere temperature = 752 F

T_w = Inside wall temperature

T_c = Temperature at interface of brick and insulation

T_s = Outside surface temperature

T_∞ = Ambient temperature = 70 F

L_1 = Thickness of concrete = 1 ft

L_2 = Thickness of insulation = 4 inches

k_1 = Thermal conductivity of concrete = 12 $\frac{BTU}{ft\ hr\ ^oF}$

h_i = Inside heat transfer coefficient ($\frac{BTU}{ft^2\ hr\ ^oF}$)

k_2 = Thermal conductivity of insulation = 0.05 $\frac{BTU}{ft\ hr\ ^oF}$

h_o = Outside heat transfer coefficient ($\frac{BTU}{ft^2\ hr\ ^oF}$)

Assume the hot gases are circulated in the room at a velocity of 20 MPH and the outside wind velocity is 10 MPH. Then h_i = 7.30 and h_o = 4.60. The overall heat transfer coefficient and heat flux can now be calculated.

$$U = \frac{1}{\frac{1}{h_i} + \frac{L_1}{k_1} + \frac{L_2}{k_2} + \frac{1}{h_o}} = \frac{1}{\frac{1}{7.3} + \frac{1\ ft}{12} + \frac{4/12\ ft}{0.05} + \frac{1}{4.60}}$$

U = 0.141 BTU/ft^2 hr F

q/A = $U\Delta T$ = 0.141 (752-70) = 96 BTU/ft^2 hr

Solving for T_w, T_c and T_s:

q/A = h_i (T_I-T_w)

96 = 7.3 $(752-T_w)$

T_w = 739 F

q/A = $\frac{k_1}{L_1}(T_w-T_c)$

96 = 12 $(739-Tc)$

T_c = 731 F = 388 C

q/A = h_o (T_s-T)

96 = 4.6 (T_s-70)

T_s = 91 F

For a wall midpoint temperature of 735 F $(\frac{739+731}{2})$, the heat required to bring the walls and ceiling to a steady-state temperature is:

$$Q_{wall,ceiling} = mCp\Delta T$$
$$= 1 \text{ ft thick} \times (60x30 + 2x30x25 + 2x60x25) \text{ ft}^2$$
$$\times 0.19 \text{ BTU/lb F} \times 120 \text{ lb/ft}^3 \times (735-70 \text{ F})$$
$$= 95.5 \times 10^6 \text{ BTU}$$

The heat required to bring the floor to steady-state temperature is calculated as follows. The temperature gradient in the concrete is illustrated below:
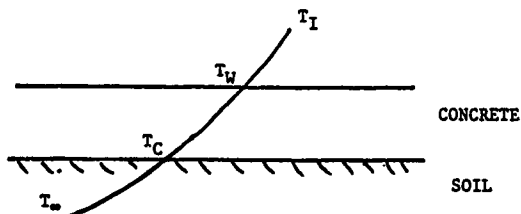
Assume 1 ft of sandy loam (10 percent water) will serve as the heat sink (k=1.08). Then:

$$U = \frac{1}{\frac{1}{7.3} + \frac{1 \text{ ft}}{0.7} + \frac{1}{1.08}} = 0.401 \frac{\text{BTU}}{\text{ft}^2 \text{ hr F}}$$

$q/A = U\Delta T = 0.401 (752-70) = 274 \text{ BTU/ft}^2 \text{ hr}$

Solving for T_w and T_c:

$T_w = 714$ F

$T_c = 323$ F

Midpoint T = 519 F

The heat required for the floor is:

$$Q_{floor} = mC_p\Delta T$$
$$= 1 \times (60x30) \times 144 \times 0.21 \times (519-70)$$
$$= 24.4 \times 10^6 \text{ BTU}$$

The contents of the building which must be heated include the steel equipment and the atmosphere. To heat the atmosphere:

Volume of air = 60x30x25 = 45,000 ft^3

Average density of air = $\frac{0.075+0.033}{2}$ = 0.054 lb/ft^3

Average Cp of air = $\frac{0.240+0.256}{2}$ = 0.248 BTU/lb F

Q_{air} = mCpΔT = 45,000 x 0.054 x 0.248 x (752-70)

Q_{air} = 0.4x10^6 BTU

To heat the equipment:

$Q_{equipment}$ = mCpΔT

$\qquad\qquad$ = 10 tons x 2000 x 0.113 x (752-70)

$\qquad\qquad$ = 1.5 x 10^6 BTU

The building heat duty is then:

$Q_{building}$ = Q_{walls} + Q_{floor} + Q_{air} + $O_{equipment}$

$\qquad\qquad$ = 95.6x10^6 + 24.4x10^6 + 0.4x10^6 + 1.5x10^6

$\qquad\qquad$ = 121.8x10^6 BTU

During heating and maintaining the building at the desired temperature for the prescribed period of time, heat will be lost to the environment. The heat loss is calculated as follows. Heat loss to ground (conduction only):

q_{ground} = 274 BTU/ft^2 hr x (60x30) = 493,000 BTU/hr

Heat loss to ambient air:

q_{air} = $q_{radiation}$ + $q_{natural\ convection}$ +

$q_{forced\ convection}$ + $q_{conduction}$

q_R = 0.1713 x 10^{-8} A ε (T_s^4 - T_∞^4)

A = area = 2(30x25) + 2(60x25) + (30x60) = 6300 ft^2

ε = emissivity = 0.85 (estimated)

T_s = 91 F = 551 R

T = 70F = 530 R

q_R = 122,000 BTU/hr

q_N = A x 0.548 x [$\frac{\rho^2 g\beta C_p k^3}{\mu\ L}$] [T_s-T_∞]$^{5/4}$

where ρ = 0.0764 lb/ft^3 (air at 70 F)

$\quad\quad$ g = 32.174 ft/sec^2

$\quad\quad$ β = 1.92x10^{-3} F^{-1}

$\quad\quad$ Cp = 0.240 BTU/lb F

$\quad\quad$ m = 1.21 x 10^{-5} lb/ft sec

$\quad\quad$ k = 0.0146 BTU/ft hr F

$\quad\quad$ L = 25 ft (height of building)

q_N = 5000 BTU/hr

q_F = 96 BTU/ft^2 hr x 6300 ft^2 = 605,000 BTU/hr

q_c = neglect (much less than q_R or q_F)

q_{air} = 122,000 + 5000 + 605,000 = 732,000 BTU/hr

$q_{heat\ loss}$ = q_{ground} + q_{air} = 493,000 + 732,000 =

$\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ 1.2 x 10^6 BTU/hr

$\quad\quad$ The time required for maintaining a supply of hot gas to the building includes heat up time and temperature maintenance time. Heat up time can be calculated by unsteady state heat conduction as follows. For one dimensional heat conduction the following equation applies:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial x^2}$$
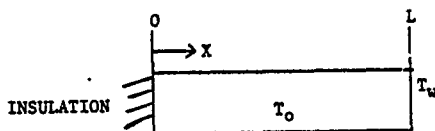
The above diagram illustrates the boundary conditions. To simplify the solution, the following definitions are made:

$\quad\quad$ θ = T-T_o

$\quad\quad$ V = T_w-T_o

$\quad\quad$ where T_o = initial temperature (70 F)

$\quad\quad\quad\quad$ T_w = wall temperature at time 0 (714 F)

The solution is:

$$\theta = V\sum_{n=o}^{\infty} (-1)^n \text{erfc} \; \frac{(2n+1)L-x}{2\sqrt{\alpha\tau}} + V\sum_{n=o}^{\infty} (-1)^n \text{erfc} \; \frac{(2n+1)L+x}{2\sqrt{\alpha\tau}}$$

where erfc = complimentary error function

α = thermal diffusivity (ft^2/hr)

t = time (hour)

L = thickness of slab (ft)

At X=0, the above equation reduces to:

$$\frac{\theta}{2V} = \sum_{n=o}^{\infty} (-1)^n \text{erfc} \; \frac{(2n+1)L}{2\sqrt{\alpha\tau}}$$

For brick, $\alpha = 0.219$ ft^2/hour, $L = 1$ foot and assume t=16 hours. Then:

$\frac{\theta}{2U}$ = erfc (0.4362) − erfc (1.3086) + ...

$\frac{\theta}{2V}$ = 0.5375 − 0.0644 = 0.4731

$1/2 \left(\frac{T-70}{731-70}\right)$ = 0.4731

$T = 695$ F

The calculated wall temperature at steady state was 731 F. Thus, about 6 hours are required to bring the building to approximately steady-state conditions. The time required to maintain the temperature can be taken from the time versus temperature graphs for thermal decomposition of explosives. After heating at 350 C for 2 hours all explosives of interest will be 99.99+ percent decomposed (see Figures 9-11). The total heating time is then 6 hours + 2 + 2 (contingency) = 10 hours.

The total amount of heat required is given as:

Q_{total} = $Q_{building}$ + q_{heat} loss x heating time

Assuming heat loss during the heat-up stage is one-half the steady-state heat loss:

$Q_{total} = 121.8 \times 10^6 + 1.2 \times 10^6 \times 6 + 1.2 \times 10^6 \times 4 =$
130.2×10^6 BTU

The overall heat duty is:

$$q_{overall} = \frac{130.2 \times 10^6 \text{ BTU}}{10 \text{ hours}} = 13 \times 10^6 \text{ BTU/hr}$$

If combustion of kerosene is the source of the hot gases then a burner capable of handling 217 gallons/hour (13x10^{6} BTU/hr ÷ 120,000 BTU/gal ÷ 0.50 (efficiency)* is required. Since burners this size are commercially available, the use of hot gases to decontaminate a brick building is feasible.

7.1.6.1.2 Blast Concrete Building

For a building comprised of 2 foot thick blast concrete walls and ceiling on a 1 foot thick concrete pad similar calculations can be performed as were done for the brick building. Prior to performing the calculation a basis for the blast concrete structure must be specified. The following configuration will be assumed:
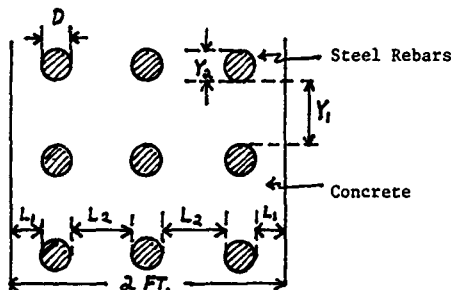
- 1 inch diameter steel rebars spaced 2 inches on center in three rows as shown above
- $L_1 = 2$ in.; $L_2 = 5\text{-}1/2$ in.; $D = y_2 = 1$ in.; $y_1 = 1$ in.
- $k_{concrete} = 0.7$ BTU/ft hr F
- $k_{steel} = 24.8$ BTU/ft hr F

Per linear foot, the thermal resistance will be:

$$\sum R_T = \frac{2L_1}{6k_c(y_1+y_2)} + \frac{3D}{6(k_c y_1 + k_s y_2)} + \frac{2L_2}{6k_c(y_1 + y_2)}$$
$$= 0.48 + 0.02 + 1.31 = 1.81 \text{ ft}^2 \text{ hr F/BTU}$$

---

* 50 percent efficiency assumes that the hot gases utilize half of their sensible heat to heat the building with the remainder vented from the building with the exhaust gases.

The density of the composite is:

$$c = \frac{488[18\frac{(\pi(1/12)^2)}{4}] + 144[2-18\frac{(\pi(1/12)^2)}{4}]}{2} = 161 \frac{lb}{ft^3}$$

The specific heat of the composite is:

$$Cp = 0.15 \text{ (wt fraction steel)} \times 0.113 + 0.85 \times 0.21$$

$$= 0.195 \text{ BTU/lb F}$$

The heat duty is calculated as follows:

$$U = \frac{1}{\frac{1}{h_i} + \Sigma Rt + \frac{L2}{k_2} + \frac{1}{h_o}} = \frac{1}{\frac{1}{7.3} + 1.81 + \frac{4/12}{0.05} + \frac{1}{4.6}}$$

$$U = 0.113 \text{ BTU/ft}^2 \text{ hr F}$$

$$q/A = 77 \text{ BTU/ft}^2 \text{ hr}$$

$$T_w = 741 \text{ F}$$

$$T_c = 602 \text{ F}$$

$$T_s = 87 \text{ F}$$

$$Q_{walls,ceiling} = 2 \text{ ft thick} \times 6300 \times 0.195 \times 161 \times$$
$$[(741+602)/2 - 70]$$
$$= 237.9 \times 10^6 \text{ BTU}$$

$$Q_{floor} = 24.4 \times 10^6 \text{ BTU}$$
$$Q_{air} = 0.4 \times 10^6 \text{ BTU}$$
$$Q_{equipment} = 1.5 \times 10^6 \text{ BTU}$$
$$Q_{building} = 264.2 \times 10^6 \text{ BTU}$$

The heat loss is calculated as follows:

$$q_{ground} = 493,000 \text{ BTU/hr}$$
$$q_{air} = 593,000 \text{ BTU/hr}$$
$$q_{heat\ loss} = 1.1 \times 10^6 \text{ BTU/hr}$$

The thermal diffusivity of blast concrete is $\alpha = \frac{}{161 \times 0.195} = 0.035 \text{ ft}^2/\text{hr}$. For L=2 ft and assuming a heat up time of 4 days:

$$\frac{\theta}{2V} = \text{erfc} (0.5455) - \text{erfc} (1.6366) + \ldots$$
$$1/2 [\frac{T-70}{(741-70)}] = 0.4405 - 0.0210 = 0.4195$$
$$T=633 \text{ F}$$

Since the steady state temperature was only 602 F, a heat up time of less than 4 days is required, say 90 hours. The total time is 90 hours + 2 hours + 8 hours (contingency) = 100 hours. The overall heat duty is:

$$Q_{total} = 264.2 \times 10^6 + \frac{1.1 \times 10^6}{2} \times 90 + 1.1 \times 10^6 \times 10$$
$$= 324.7 \times 10^6 \text{ BTU}$$

$$q_{overall} = \frac{324.7 \times 10^6}{100} = 3.2 \times 10^6 \text{ BTU/hr}$$

Thus, hot gases may be used to decontaminate a reinforced concrete building.

7.1.6.1.3 Wood Building

For a building comprised of 5/8 inch plywood and 2x6 inch wood studs walls and ceiling on a 1 foot thick concrete pad similar calculations can be performed as were done for the brick building. Prior to performing the calculations, a basis for the wood structure must be specified. The following configuration will be assumed:
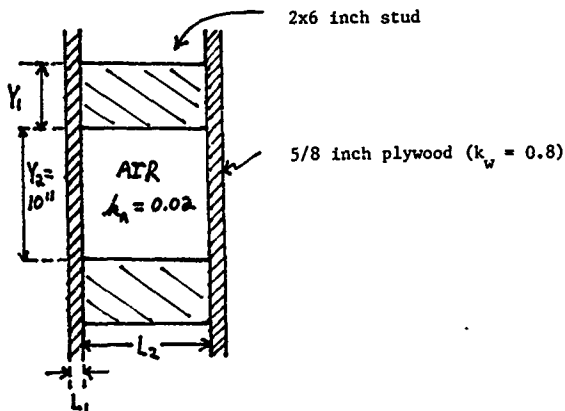
Per linear foot, the thermal resistance will be:

$$\sum R_T = \frac{2L_1}{k_w(y_1 + y_2)} + \frac{L_2}{k_w y_1 + k_A y_2}$$

$$= \frac{2 \times 5/8}{0.8(2 + 10)} + \frac{6}{0.8 \times 2 + 0.02 \times 10} = 3.46 \text{ ft}^2 \text{ hr F/BTU}$$

For each square foot of surface area, the wall will contain $(2 \times 5/8/12) + (2/12) \times (6/12) = 0.188$ ft^3 of wood and $(10/12) \times (6/12) = 0.417$ ft^3 of air. The heat duty is calculated as follows:

$$U = \cfrac{1}{h_i + \sum Rt + \cfrac{L2}{k2} + \cfrac{1}{h_o}} = \cfrac{1}{\cfrac{1}{7.3} + 3.46 + \cfrac{4/12}{0.05} + \cfrac{1}{4.6}}$$

$U = 0.095$ BTU/ft^2 hr F

$q/A = 65$ BTU/ft^2 hr

$T_w = 743$ F

$T_c = 518$ F

$T_s = 84$ F

$Q_{walls+ceiling} = 6300$ ft^2 × $[0.188 \times 34 \times 0.29 + 0.417 \times 0.075 \times 0.24]$ ×

$$[(743+518)/2 - 70]$$

$= 6.6 \times 10^6$ BTU

$Q_{floor} = 24.4 \times 10^6$ BTU

$Q_{air} = 0.4 \times 10^6$ BTU

$Q_{equipment} = 1.5 \times 10^6$ BTU

$Q_{building} = 32.9 \times 10^6$ BTU

The heat loss is:

$q_{ground} = 493,000$ BTU/hr

$q_{air} = 494,000$ BTU/hr

$q_{heatloss} = 1.0 \times 10^6$ BTU/hr

The heat-up time will primarily depend on the time required to heat the air between the plywood sheets. For air $\alpha = 1.11$. Assume a time of 1/2 hour then:

$\cfrac{\theta}{2V} = $ erfc (0.3356) - erfc (1.0067) + erfc (1.6779)

$\cfrac{1}{2}$ [$\cfrac{T-70}{743-70}$] $= 0.6353 - 0/1548 + 0.0179 = 0.4984$

$T = 741$ F

Thus, less than 1/2 hour is required to reach steady state. The total time for heating is:

0.5 hours + 2 hours + 2.5 hours (contingency) = 5 hours

The overall heat duty is calculated as follows:

$Q_{total} = 32.9 \times 10^6 + 1.0 \times 10^6$ × 0.5 + 1.0×10^6 × 4.5

$= 37.7 \times 10^6$ BTU

$q_{overall} = \cfrac{37.7 \times 10^6}{5 \text{ hrs}} = 7.5 \times 10^6$ BTU/hr

Thus, hot gases may be used to decontaminate wood buildings.

7.1.6.2   Infrared Heating

If heating is performed on one side of the building, the cal-
culations made for Hot Gases will approximate the heat required assuming
that the wall temperature is held at 700–750 F. If, however, heating is
performed simultaneously on both sides of the building, another analysis
must be performed as follows. It will be assumed that the heat duty re-
quired to bring each of the three buildings to a steady-state temperature
is the same for IR heating as for hot gases. The heat loss to the ground
will be the same as given for Hot Gases. The heat loss to the ambient air
is calculated as follows. Neglecting natural convection, forced convec-
tion (assume the space between the IR heaters and the wall is still air)
and conduction, the heat loss to the air is given as:

$$q_{air} = q_{radiation} = 0.1713 \times 10^{-8} \times 6300 \times \epsilon \times$$
$$[(752+460)^4 - (70+460)^4]$$
$$= 22.4 \times 10^6 \, \epsilon \, BTU/hr$$

For an average emissivity for the building materials of 0.9:

$$q_{air} = 20.2 \times 10^6 \, BTU/hr$$

$$q_{heat \, loss} = 2 \, sides \times q_{air} + q_{ground}$$
$$= 2 \times 20.2 \times 10^6 + 0.5 \times 10^6 = 40.9 \times 10^6 \, BTU/hr$$

The following boundary conditions apply for solution of the un-
steady state heat transfer by heating simultaneously on both sides of a
wall or ceiling:
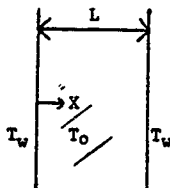
The solution is

$$\frac{T - T_W}{T_0 - T_W} = \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \, SIN \left(\frac{n\pi}{L}\right) x \quad \exp -\left(\frac{n\pi}{2}\right)^2 F_0$$

where T_w = Wall temperature = 752 F

T_o = Initial temperature = 70 F

T = Temperature at X at time t

L = Width of building material

$F_o = \dfrac{\alpha\tau}{(L/2)^2}$

$n = 1,3,5,\ldots$

For $X = \dfrac{L}{2}$ (midpoint), $\alpha = 0.219$ ft^2/hr (brick) and a time of 0.5 hours, the midpoint temperature will be at 744 F. For a heating time of 1/4 hour, the midpoint will be at 735 F. Thus, a time of about 1/4 hour is required to near steady-state temperatures in brick. For a 2 ft wall of blast concrete a heating time of 1 hour is required whereas only several minutes are required for the wood building.

Since the temperature is so high throughout the building material (375 C), all explosives should be thermally decomposed as soon as heat-up is accomplished. Thus, the total heating time is 1/4 hour for brick, 1 hour for blast concrete and several minutes for wood.

The total heat required is:

Q_{total} (brick) = 121.8x10^6 + 0.25 hr/2 x 40.9 x 10^6

$\qquad\qquad$ = 126.9x10^6 BTU

Q_{total} (blast concrete) = 264.2x10^6 + 2 hr/2 x 40.9x10^6

$\qquad\qquad\qquad$ = 305.1x10^6 BTU

Q_{total} (wood) = 32.9x10^6 + 0.1/2 x 40.9x10^6

$\qquad\qquad$ = 34.9x10^6 BTU

If an entire building is heated at one time, the power requirements may not be able to be attained since q = 126.9x10^6 BTU / 0.25 hr = 507x10^6 BTU/hr = 149 megawatts. Assuming a power capacity of 10 megawatts, the building area that can be heated at one time is:

$\dfrac{10\text{X}1000\text{X}3412}{\frac{126.9\text{x}10^6}{6300}}$ = 1700 ft^2 for the brick building, or

705 ft^2 for the blast concrete building, or 6100 ft^2 for the wood building.

Thus, infrared heating is feasible for building decontamination if heating is performed in building sections rather than as a whole.

7.1.6.3 Flaming

The feasibility of flaming as a sub-surface decontamination method is dependent on the dwell time of the flame on the surface. A long dwell time is preferred to allow heating of the sub-surface by conduction. However, a long dwell time (minutes) is also detrimental because of material damage due to the high thermal gradient.

The dwell time of the flame on a building may be determined as follows: For one-dimensional heat conduction into a slab, the heat transfer equation that must be solved is:

$$\frac{\partial T}{\partial t} = \alpha \, \frac{\partial^2 T}{\partial Y^2}$$

where T = temperature

t = time

Y = penetration depth

α = thermal diffusivity of the building material

Applying the boundary conditions shown in the diagram below, a solution can be obtained.
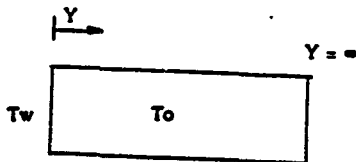
$$\frac{T - T_w}{T_o - T_w} = \text{erf} \left(\frac{Y}{\sqrt{4\alpha t}} \right)$$

where T_w = constant wall temperature at Y = 0 (assume T_w = 1500 F)

T_o = initial slab temperature (F)

T = temperature at depth y (F)

Y = depth into slab (ft)

α = thermal diffusivity (ft^2/hr)

t = time (hours)

erf = error function

To achieve a thermal penetration of 300 C at a depth of two inches, the following flame dwell times are required:

Material	Dwell Time
Blast Concrete	16.2 minutes*
Brick	2.6 minutes
Wood	**

Because of the long dwell time required for a thermal penetration of only two inches, flaming should be considered only as a near surface decontamination concept. Thus, as compared with hot gases and IR heating which have the potential to heat all the way through a building material, flaming is less advantageous and is eliminated ı om further evaluations.

* A dwell time of 144 minutes is required for a 6 inch thermal penetration depth.

** Flaming is not recommended on wood.

7.2 ABRASIVE REMOVAL OF EXPLOSIVES

7.2.1 Introduction

An abrasive concept is one in which some device is used to re-
move surface layers of contaminated building materials. The surface
layers containing the contaminants are collected and then processed.
Abrasive methods are particularly suited to decontaminate buildings where
the depth of contaminant penetration into the building materials is less
than 1 to 2 inches. Removal of surface layers to a depth greater than two
inches is possible with several of the abrasive concepts, however, the
building would probably become structurally weakened. An exception to
this would be reinforced concrete blast walls; the rebars would probably
have to be removed if a removal depth greater than 1 to 2 inches is de-
sired. Demolition of the building can be used to decontaminate buildings
in which the depth of contaminant penetration is greater than 1 to 2
inches. It is important to note that selection of the optimum abrasive
techniques is dependent upon the depth of contamination.

Various abrasive decontamination methods were identified during
this program. These concepts were developed and then screened to elim-
inate the least advantageous. The selected concepts were then analyzed in
engineering terms to determine their physical limitations and feasibil-
ities. Several hypothetical structures derived from information obtained
in the Site Surveys were used as the basis for determining feasibility.
Finally, a cost analysis was performed on the concepts with the greatest
potential for complete decontamination of the hypothetical structures.

7.2.2 Abrasive Concept Descriptions

The following are short descriptions of the abrasive concepts.
Detailed descriptions are given in Appendix III.

7.2.2.1 Electropolishing

Electropolishing is a commonly used electrochemical process that has been effectively employed for decontamination purposes. A contaminated metal object serves as the anode in an electrolytic cell. The passage of electric current results in the anodic dissolution of the surface material and, with proper operating conditions, a progressive smoothing of the surface. Contaminants on the surface or entrapped within surface imperfections are removed and released into the electrolyte by this surface dissolution process. The production of a polished surface also facilitates the removal of residual electrolyte by rinsing.

Advantages
o Highly effective in removing contaminants from metal surfaces.

Disadvantages
o Application limited to metallic materials.
o Metal surface must be unpainted.

See Section 7.5 for a discussion of the specific applicability of this concept.

7.2.2.2 Acid Etch

Acid is applied to a surface to promote corrosion. Neutralization and removal of the surface layer follows. The debris is then neutralized and decontaminated.

Advantage
• May cause decomposition of the explosive at the same time it is removed from the surface.

<u>Disadvantages</u>
- o Removal of a portion of the metal may weaken the structure.
- o Hazardous operation requires special application equipment.
- o Primarily applicable to metals which will readily corrode.
- o Large material requirement.

7.2.2.3 Scarifier

The scarifier technique is capable of removing approximately one inch of surface layer from concrete or similar materials. The scarifier tool consists of pneumatically operated piston heads that strike a surface causing concrete to chip off. The piston heads consist of multi-point tungsten carbide bits.

<u>Advantages</u>
- o Can achieve a deeper penetration (removal) of surface as compared with most other surface removal techniques.
- o Suitable to both large open areas and small area application due to availability of hand-held version.

<u>Disadvantages</u>
- o The treated surface retains a rough appearance that would probably require resurfacing.
- o Substantial amounts of contaminated debris generated which requires further processing.
- o Only effective as a near surface removal technique.
- o May detonate pockets of explosive residue.

7.2.2.4 Sandblasting

Sandblasting is an abrasive surface removal technique in which an abrasive such as sand or steel pellets are used to uniformly remove building material layers containing the contaminants.

Advantages
o Sandblasting is a widely used surface removal technique.
o It can simultaneously and readily remove paint and
  contaminants in close proximity to the surface.
Disadvantages
o Large amount of explosive laden dust and debris generated.
o Only effective as near surface treatment.
o Potential for detonation of pockets of explosive.

7.2.2.5 Demolition

Mechanical demolition involves manual total destruction of a
building followed by removal of debris to either a landfill or for decon-
tamination.

Advantages
o Demolition allows for decontamination of building materials
  that have been completely permeated by explosives.
Disadvantages
o The building is destroyed.
o Huge quantities of debris must be decontaminated.
o Airborne contamination may occur.
o Potential risk of detonation of pockets of explosive.

7.2.2.6 Drill and Spall

The drill and spall technique is capable of removing approx-
imately 2 inches of surface layer from concrete or similar materials. The
technique consists of drilling holes (1 to 1-1/2 inches diameter) approx-
imately 3 inches deep into the surface. The spalling tool bit is inserted

into the hole and hydraulically spreads to spall of the contaminated concrete.

Advantages
o The technique can achieve deeper penetration (removal) of surfaces as compared with other surface removal techniques.
o Good for large scale application.

Disadvantages
o Only effective as a surface treatment of concrete.
o The treated surface retains a very rough appearance that would necessitate resurfacing.
o Substantial amounts of contaminated debris require processing.
o Potential for detonation of pockets of explosives.

7.2.2.7 Ultrasound

Ultrasonic cleaning is a surface scrubbing technique that can be employed to remove surface contaminants. Small equipment would be removed and loaded into ultrasonic cleaning tanks. Specially designed scrubbers would then be used to clean the walls and floors. An ultrasonic cleaning system typically consists of an ultrasonic generator, a transducer, a cleaning tank, a liquid coupling agent solvent and a heater. The generator converts line power from 60 Hz to a higher frequency, i.e. 18 to 90 KHz. The transducer then converts these high frequency impulses to low amplitude mechanical energy waves of the same frequency. The warm liquid coupling agent (150-170 F) serves to transmit this energy to the object to be cleaned. The compression-rarefaction-compression wave cycle transmitted by the generator causes the liquid to cavitate and implode creating minute quantities of energy with tremendous localized force. Pressures and temperatures can reach approximately 10^4 psi and 10^4 C. These imploding cavities serve to scrub the surface being decontaminated causing spalling and descaling (Kirk-Othmer, 1969).

Advantages
o Potentially applicable to all building materials.
o Paint removal is not required prior to cleaning.
o Localized high temperature may cause decomposition of some
  explosives.

Disadvantages
o Only known to be effective as a surface removal technique.
o The couplant may carry the contaminant deeper into porous
  materials.
o The cleaning liquid and removed surface must be
  decontaminated and disposed.

See Section 7.5 for a discussion of the specific applicability of this
concept.

7.2.2.8 Cryogenics

The surface of the building material is exposed to cryogenic
temperatures in order to make it brittle. The surfaces are then chipped
or scraped off by, for example, pneumatic hammers.

Advantages
o The cold surfaces are very brittle and therefore may be
  removed easily.
o The cold may desensitize otherwise sensitive explosives.

Disadvantages
o Potential for uneven surface removal.
o Difficult application on hard-to-reach areas.
o High cost of cryogenic fluid (large quantities required).
o Labor intensive.

7.2.2.9 Hydroblasting

A high pressure (500-20,000 psi) water jet impacts the surface removing the contaminated surface. Surface debris and water is then collected and decontaminated.

Advantages
o Hydroblasting offers a relatively inexpensive, non-hazardous surface decontamination technique using off-the-shelf equipment.
o Hydroblasting can very easily incorporate variations such as hot or cold water, abrasives, solvents, surfactants, and varied pressures.
o Many manufacturers produce a wide range of hydroblasting systems and high pressure pumps.

Disadvantages
o Hydroblasting may not effectively remove contaminants that have penetrated the surface layer.
o Large amounts of water will have to be collected and treated.

7.2.2.10 Vacu-Blast

Vacu-blasting entails removal of the surfaces of a building through a sandblasting technique where all dust, debris and used abrasive are vacuum returned to an over/under particle separator and the abrasive continuously recycled.

Advantages
o Vacu-blasting is a widely used surface removal technique.
o It can simultaneously remove paint and contaminants from surface layers.

o All dust, debris and abrasive are contained using a vacuum
   system.
o The abrasive is separated from the debris and reused.
Disadvantages
o Only effective as a surface treatment.
o Collected debris must then be decontaminated and disposed of.
o The abrasive force may detonate residues of primary
   explosives.

7.2.3 Concept Evaluation

A summary of the evaluation scores for each of the abrasive
concepts is given in Table 21. The following procedure was used to screen
for the better concepts.

1) Any concept with a total score of zero or less is
   eliminated. Thus, Cryogenics, Ultrasound, Drill
   and Spall, and Electropolishing are eliminated.

2) Any concept which scores a double minus (--) in Safety,
   Penetration Depth, or Applicability To Complex Surfaces is
   eliminated. Thus, the Acid Etch and Demolition Concepts
   are eliminated.

3) If the total score for the operating and capital costs is
   less than zero, then the concept is eliminated. This does
   not eliminate any concepts.

Thus, the only remaining concepts after this screening are
Hydroblast, Vacublast, Sandblast, and Scarifier.

TABLE 21. ABRASIVE DECOMPOSITION OF EXPLOSIVES CONCEPT EVALUATION

Criteria	Vacu-Blast	Hydro-Blast	Acid Etch	Sand-Blast	Scarifier	Demolition	Cryogenics	Ultra-Sound	Drill and Spall	Electro-Polish
Safety	++	+	-	-	++	--	-	+	+	-
Damage to Building	+	++	++	++	+	--	+	++	+	++
Penetration Depth	+	-	--	-	+	++	+	--	+	--
Applicability to Complex Surfaces	+	+	++	+	-	++	-	--	--	--
Operating Costs	+	++	++	++	-	+	-	+	--	-
Capital Costs	+	++	++	++	++	++	++	+	+	++
Waste Treatment Costs	-	-	-	-	-	--	-	-	--	--
TOTAL	+6	+6	+4	+4	+3	+1	0	-2	-2	-4

7.2.4   Engineering Analysis

7.2.4.1   Hydroblasting

The hydroblaster, also called "hydrolaser", has been success-
fully used to decontaminate nuclear facility equipment such as pump
internals, valves, cavity walls, spent fuel pool racks, reactor vessel
walls and head, fuel handling equipment, feedwater spargers, floor drains,
sumps, interior surfaces of pipes and storage tanks (Manion, 1980). A
hydroblaster can generate a water pressure of up to 50,000 psi allowing
easy removal of most surfaces. For example, a hydrolaser can remove 1/8
to 1/4 inch of concrete surface at the rate of approximately 360 square
feet per hour. This technique is superior to sandblasting which removes
surfaces at the rate of approximately 375 square feet per day.

Water from the hydrolaser can be sprayed on all surfaces ex-
pected to be encountered and can effectively remove them. However, if
the depth of contamination is greater than about 1/4 inch in porous mate-
rials, the effectiveness of complete decontamination by hydroblasting
would be questionable.

A key advantage to hydroblasting over other abrasive methods is
that the potential for explosions is reduced. This is demonstrated by the
use of high pressure water (4000 psi) in the Cavijet process where TNT and
Composition B are washed out of projectiles (Conn, 1979).

Key disadvantages to this technique include 1) the generation of
a large amount of contaminated mist, 2) formation of contaminated rubble
and 3) production of a large volume of water which will require treatment
to decompose contaminants. It may be preferable to use a mixture of water
and decontaminating solution so any "loose" explosive would be decontam-
inated on contact. The volume of water can be substantially reduced if it
can be recycled following removal of solid particulates. Thus, with these
modifications hydroblasting is a viable candidate method for facility de-
contamination.

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7.2.4.2 Sandblasting

ʂan .blasting* is an extensively used technique for removal of
rust., ɔɑɪᵔr, scale, etc. in a variety of applications including shipyards,
ref ʲˀɹɪ ɟ, chemical plants, buildings or other complicated structures of
large square foot areas. (Plaster, 1964). The versatility of sandblasting
lies in its ability for surface removal in complex areas. Since the sand
is sprayed onto the surfaces, most otherwise inaccessible areas can be
decontaminated by surface removal. With modifications the sandblaster can
be adapted for use on the inside of pipes and tanks. Another versatility
to sandblasting is the wide range of materials that can be cleaned in-
cluding brick, cement, metals**, concrete block, terra cotta and, pos-
sibly, wood. Sandblasting transite, a major construction material of many
explosive plants, does not appear feasible because of the large quantity
of airborn asbestos particles which will undoubtedly be generated.

A major drawback to sandblasting is the large quantity of
abrasive required. Typically 6 tons of abrasive are required per unit per
day. Recycle of the abrasive is possible if the abrasive and debris gen-
erated during a days activities is either screened (over/under separator)
or passed through a cyclone. However, this would only be feasible if the
contaminated debris could be completely separated from the abrasive.
Otherwise, there is potential for uncontaminated areas to become contam-
inated. Another difficulty encountered in recycling abrasive is that the
abrasive can adsorb water which usually results in clogging of the
abrasive feeder (Plaster, 1964).

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* Other abrasives other than sand can be used including cut wire,
pellets, steel shot, steel grit, garnet or alumina.

** 0.02 lb/min of steel can be removed while sandblasting at 70 psi
(Plaster, 1964).

Overall, sandblasting is a slow method for surface removal. Godfrey (1982) quotes that an area of 375 squre feet per eight hour day can be sandblasted. Since the apparatus requires two operators – one to perform the actual sandblasting and the other to control the unit and regulate the feed, only a total of 375/2x8 = 23 square feet can be sand-blasted per manhour.

A key knowledge gap which must be addressed prior to the selec-tion of sandblasting for explosive facility decontamination is whether or not an explosion would result when contaminated building materials are sandblasted. If an explosion can occur then sandblasting loses its util-ity since the explosive contaminants would require desensitization prior to sandblasting.

A second knowledge gap, equally as important, is the depth of contamination in the building materials. If a contamination depth greater than about 1/4 to 1/2 inch is encountered then sandblasting cannot be em-ployed to completely decontaminate the building. If, however, the depth of penetration is less than about 1/4 inch then sandblasting is a viable decontamination method.

7.2.4.3 Vacu-blasting

Vacu-blasting is essentially a modification of sandblasting where the abrasive is continuously collected and recycled (see Figure 12). The major advantages to vacu-blasting over sandblasting is the reduction in the quantity of abrasive required* and the reduction in airborne par-ticulates and debris. Thus, in addition to the materials mentioned for sandblasting, transite may be vacu-blasted because most of the asbestos fibers would be continuously vacuum collected.

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* Only 300 lbs of abrasive are required per unit per day.
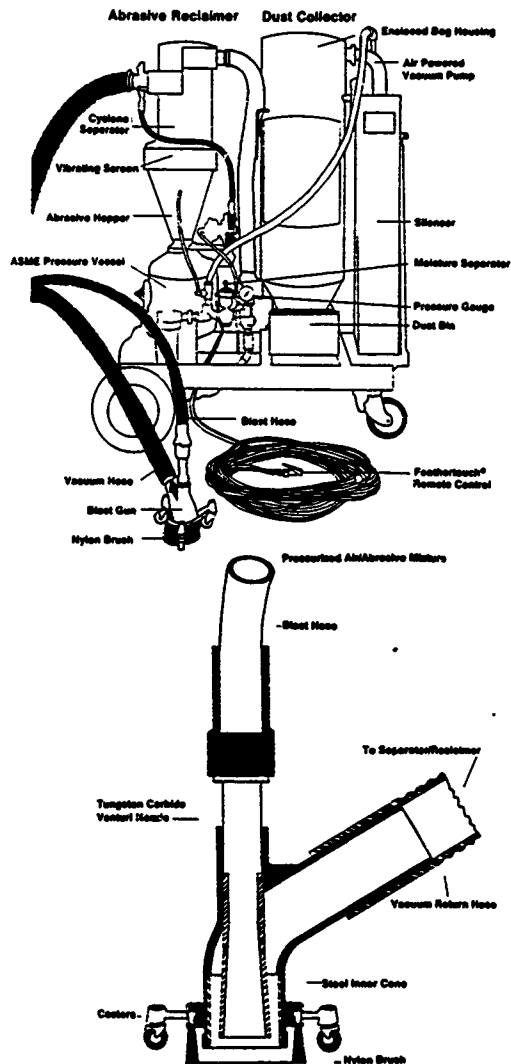
FIGURE 12.   VACU-BLAST APPARATUS (MANUFACTURER'S BROCHURE)

The major disadvantage to vacu-blasting is that the method is primarily applicable to open, obstruction-free areas. However, several different nozzle designs are available which allow cleaning of building corners, and the external surfaces of pipes. The internal surfaces of pipes can be vacu-blasted by connecting one end to the pressurized abrasive hose and the other to the vacuum return hose (Plaster, 1964). The key difficulties in vacu-blasting would arise in cleaning of the inside of tanks, sumps, behind pipes, etc. Thus, the versatility of vacu-blasting is substantially reduced as compared with sandblasting. Another disadvantage to vacu-blasting is that since the abrasive is not sprayed on, as is the case in sandblasting, more time would be required to cover the same surface area.

Thus, although vacu-blasting is more advantageous than sandblasting in regards to reduction in airborne particulates and abrasive requirements, it is less advantageous in terms of versatility and labor cost. As with sandblasting, the potential for an explosion and depth of contamination during vacu-blasting and depth of contamination must be addressed prior to selection of vacublasting as a decontamination method.

7.2.4.4 Scarifier

The scarifier, a pneumatically operated surface remover, can strip off layers of concrete up to a depth of one inch. Various units are commercially available that can be used for wall and floor application as shown in Figure 13. The key benefit of the scarifier is that much greater depths of removal are possible than with either sand or vacu-blasting. However, the primary disadvantages of the scarifier appear to outweigh the benefits in that the use of a scarifier is restricted to concrete and can only be used in open areas free of obstruction.

The scarifier would have some limited applicability if the structures encountered in explosive manufacturing plants were composed primarily of concrete. However, structures/explosives contaminated are
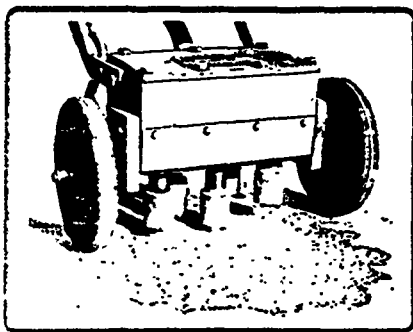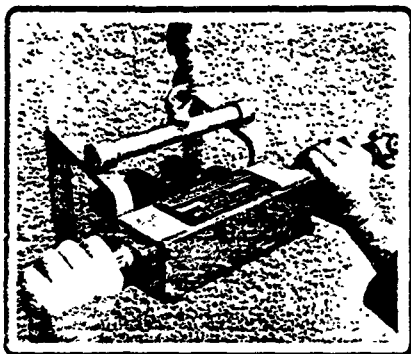
FIGURE 13.   WALL AND FLOOR SCARIFIERS
(MANION, 1980)

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generally constructed with a composite of building materials (i.e. concrete floor, brick walls, wood ceiling).* Since the porosity and permeability of these building materials (e.g. concrete and brick) are similar, it is expected that the depth of penetration of contaminants would also be similar. Thus, a method other than the scarifier which would remove surfaces to the desired depth from brick and other materials would be required. Since the disadvantages outweigh the benefits, the scarifier concept is eliminated from further discussion.

7.2.5 Summary

Table 22 lists the applicability of the abrasive concepts discussed in this section. Cost analyses were performed for all concepts except the Scarifier Concept.

TABLE 22. APPLICABILITY OF SELECTED ABRASIVE CONCEPTS

Selected Concept	Material Applicability	Anticipated Removal Depth
Sandblasting	Potentially all materials	<1/4 inch
Vacu-blasting	Potentially all materials	<1/4 inch
Scarifier	Concrete only	>1 inch
Hydroblasting	Potentially all materials	<1/4 inch

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* Information obtained from Site Surveys.

7.3   EXTRACTIVE REMOVAL OF EXPLOSIVES

7.3.1   Introduction

An extraction concept entails the use of a solvent to dissolve
the contaminants in building materials. The solvent can be either organic
or aqueous (perhaps containing surfactants) or a combination aqueous/
organic system. Application of the solvent can be performed by a variety
of methods. Following application, solvent laden with contaminants is
collected and decontaminated either by incineration or chemical treatment.
(It should be noted that several of the concepts identified in this
section can also be employed as procedures for the application of liquid
reactants.)

The performance of a solvent extraction process for building
decontamination depends highly on the nature of the diffusion of neat
solvent into porous materials and the diffusion of contaminated solvent
from the materials. At this stage it can only be speculated that the
process may work to some degree. The ultimate performance of a solvent
extraction process can only be determined by experimental study in which
the diffusion of solution into and from various building materials is
characterized. It is anticipated that a solvent extraction process will
be primarily a near surface decontamination technique. Thus, if the depth
of contamination is greater than about 1/4 to 1 inch, the feasibility of
complete decontamination of a building by a solvent extraction technique
is greatly diminished.

Various solvent extraction methods were identified during this
program. These concepts were developed and then screened to eliminate the
least advantageous concepts. The selected concepts were then analyzed in
engineering aspects to evaluate the physical feasibilities and limita-
tions. Several hypothetical structures derived from information obtained
in the field surveys were used as the basis for assessing feasibility.

Finally, a cost analysis was performed on the concepts with the greatest potential for complete decontamination of the hypothetical structures.

7.3.2 Extraction Concept Descriptions

The following are short descriptions of the extraction processes. Detailed descriptions are provided in Appendix III.

7.3.2.1 Solvent Circulation

An organic solvent such as acetone is circulated across the surface of a building solubilizing the contaminants. The spent solvent is thermally or chemically treated to decontaminate the agents. The solvent may be recycled if no degradation of the solvent occurs during treatment.

Advantages

o Removal of contaminated paint is possible if the proper solvent is selected.

o Depending on solvent-explosive compatibility, this approach may be a very efficient removal system.

Disadvantages

o Method not suited for intricate structures.

o Penetration of solvent into material matrix followed by outward diffusion may take a long time.

o Residual solvent in building material may require removal and/or decomposition.

o The solvent may tend to carry the explosive farther into the wall before outward movement occurs.

7.3.2.2 Supercritical Fluids

This method is based on the use of a supercritical fluid as a
solvent extraction medium. A supercritical fluid is one that exists when
temperature and pressure conditions are above the critical temperature and
pressure of the substance.

Advantages
o Supercritical fluids often have superior solubility proper
    ties compared to liquid solvents.
o Purification of supercritical fluids is often easier than
    conventional liquid solvents (Chemical and Engineering News,
    August 3, 1981, p. 16).
Disadvantages
o It would be difficult to maintain supercritical conditions
    for purposes of building decontamination because the critical
    pressure and/or temperature of most substances is much higher
    than atmospheric/ambient conditions. For example, CO_2 has
    a critical pressure of 72.9 atmospheres although the critical
    temperature is only 31 C. If a supercritical fluid were
    identified which exists at standard conditions, the
    extraction capabilities would have to be merited. No such
    fluid has been identified.

See Section 7.5 for a discussion of the specific applicability
of this concept.

7.3.2.3 RadKleen

Freon® 113 is sprayed under pressure on the building material.
The Freon dissolves the contaminants and is then collected and distilled
for reuse. A spray and vacuum pick-up apparatus may be employed for ap-

plication and collection of the Freon. RadKleen is an established version
of a solvent circulation process.

Advantages

o Vapors can penetrate inaccessible areas.

o Freon 113 is a stable, non-polar organic solvent suitable for
  extracting organic compounds.

o The solvent is nontoxic, nonflammable and noncarcinogenic.

o Low surface tension allows rapid wetting of the surface.

o Low viscosity allows easy particulate separation.

o Freon may be reclaimed easily when used in a closed system.
  (The cost of Freon 113 makes reclamation mandatory.)

Disadvantages

o Complete extraction of contaminants from subsurfaces may be
  difficult to accomplish.

o Diffusion may limit rate of application.

7.3.2.4 Vapor Phase Solvent Extraction

An organic solvent is heated to its boiling point and the vapors
allowed to circulate in a building. The vapors permeate porous building
materials where they condense, solubilize the explosive and diffuse out-
ward. The liquid solvent laden with contaminant is collected in a sump
and treated to permit recycle of solvent.

Advantages

o Method well suited to all areas of a building including
  intricate structures.

o Solvent permeability and diffusivity are enhanced by using
  vapor phase transport.

• Removal of contaminated paint is possible if the proper
  solvent is selected.

o Depending on the solvent-explosive compatibility it may be a
   very efficient removal system.
o Some enhanced solubility of explosives in the solvent is
   expected due to the elevated temperatures employed.

Disadvantages

o Outward diffusion of solvent laden with explosive may require
   long times.
o The solvent may tend to carry the explosove farther into the
   wall before outward movement occurs.

7.3.2.5 Surfactants

A surfactant may be added to water to lower its surface tension.
Explosives may be more soluble in such a system permitting easier removal.

Advantages

o The surfactant may allow deeper penetration of the solvent
   into contaminated materials by lowering the surface tension
   of the solvent thus assisting in physical removal.
o Surfactant/hydroblast system is currently in use for routine
   cleanup of a commercial explosive manufacturer.

Disadvantages

o Only effective as a surface or near surface decontamination
   technique.
o The low solubility of explosives in aqueous media may be only
   marginally enhanced by the use of surfactants.

7.3.2.6 Strippable Coatings

Coatings in which explosives are soluble could be applied to a
contaminated surface and subsequently removed for decontamination.

Strippable coatings have been designed that are readily removed via a simple stripping action which removes the coating as large sheets.

Advantages
o Strippable coatings contain the contaminant for easier hand ling and disposal.
o It may be possible to incorporate reactants into the coating which decontaminate the explosive prior to stripping.
o Some coatings have been designed so that they are quite flammable. Such coatings could be utilized ror explosive removal prior to incineration.

Disadvantages
o The explosives may still be active.
o The polymer would need to be formulated so that it would not bind irreversibly to the wall or item on which it is applied.

7.3.2.7 External Steam Generator

Steaming involves the use of steam to physically extract explosive contaminants from building materials. In this method the entire building would be flooded with steam from an external steam generator. Condensate would be collected in a sump for treatment.

Advantages
o This approach has minimal manpower requirements while providing a simple mechanism to clean an entire building at once.
o Depending on the contaminant, thermal decomposition and or hydrolysis may occur.
o May be effective on wood and transite.
o Increased solubility of explosives in water at elevated temperatures.

Disadvantages

o Only known to be effective for surface decontamination.

7.3.2.8 Manual Steaming

Steaming involves the use of steam to physically extract explo-
sive contaminants from building materials. The steam would be applied to
the building through hand-held wands or automated systems and the con-
densate would be collected in a sump for treatment.

Advantages

o Steam cleaning is a relatively inexpensive and simple
   mechanism used throughout the commercial explosive industry.
o Depending on the contaminant, thermal decomposition and/or
   hydrolysis may occur.
o Increased solubility of explosives in water at elevated
   temperatures.

Disadvantages

o Only known to be effective for surface decontamination.
o Labor intensive operation; costly process if automated.
o Probably only mechanical removal of explosives takes place.

7.3.3 Concept Evaluation

A summary of the evaluation scores for each of the extraction
concepts is given in Table 23. The following procedure was used to screen
for the better concepts.

1) Any concept with a total score less than zero is eliminated.
    Thus, Supercritical Fluids is eliminated.

TABLE 23. EXTRACTION CONCEPT EVALUATION

Criteria	Steam External	Surfactants	RadKleen	Strippable Coating	Vapor Circulation	Steam Manual	Solvent Circulation	Super Critical
Safety	++	++	++	+	+	-	+	-
Damage to Building	++	++	++	++	++	++	±	-
Penetration Depth	+	--	-	--	-	--	-	++
Applicability to Complex Surfaces	++	++	++	++	++	++	--	--
Operating Costs	++	++	++	++	+	++	+	--
Capital Costs	+	++	+	++	+	++	+	-
Waste Treatment Costs	-	-	-	-	-	-	-	-
	+9	+7	+7	+6	+5	+4	+1	-5

2) Any concept which scores a double minus (--) in Safety,
    Penetration Depth, or Applicability To Complex Surfaces is
    eliminated. Thus, Surfactants, Strippable Coating, Manual
    Steam and Solvent Circulation concepts are eliminated.

3) If the total score for the operating and capital costs is
    less than zero then the concept is eliminated. This does
    not eliminate any concepts.

Thus, the remaining concepts after this preliminary screening
are Radkleen, Vapor Phase Solvent Circulation and External Steaming.

7.3.4 Engineering Analysis

7.3.4.1 Vapor Phase Solvent Circulation

In the vapor circulation concept, a heated organic solvent in
which the explosives would be highly soluble (e.g., acetone) would be used
to dissolve contaminants. A vapor phase would be used to allow easy ap-
plication of the solvent simultaneously throughout the sealed building.
As the solvent condenses it dissolves contaminants. The solvent laden
with explosives is collected in a sump for treatment.

The process may entail the following steps:

Solvent is vaporized in a boiler situated in a building. Steam,
for example, can be used to supply the heat duty to vaporize the low
boiling point organic solvent. The vaporized solvent would permeate the
building and condense on the building materials dissolving contaminants as
it condenses. Repeated condensation of solvent will cause the building
material to heat up to near the boiling point of the solvent. In porous
materials such as concrete, the building would act as a condensor for the
solvent, and repeated condensation and vaporization within the porous
material would physically remove contaminants and dissolve them. The

dissolved contaminants would diffuse under a concentration gradient to the surface of the building materials where fresh solvent would serve to transport the contaminants to a sump. The contaminated solvent would then be pumped out, passed through a treatment system to remove or destroy the contaminants, and recycled to the boiler. The process could be run for days, if necessary, without prohibitive costs since personnel would only be indirectly involved in the operation (the building would be sealed).

The uncertainties remaining for this process are the length of time required for the dissolved contaminants to diffuse outward from the subsurface of porous materials and the ultimate removal efficiency that may be obtained. At this stage, it can only be speculated that the method will work. A detailed analysis of mass transfer limitations (diffusion) must be performed before this concept can either be eliminated or validated as a useful system.

It may be noted that a modification of this process may be employed in the application of selected liquid reactants. The reactant could be volatilized and allowed to permeate into the building materials. As the reactant condenses, it decomposes the contaminant. Thus, no outward diffusion limitation would be encountered as they would for the solvent extraction method. In engineering terms, this may be a preferable method over, for example, the spraying of liquid reactants because the entire building can be treated simultaneously with indirect involvement of personnel. Also, the diffusion rate of vapors into porous materials would be much greater than for liquids (if capillary action is not substantial).

7.3.4.2 RadKleen

RadKleen was developed by Health Physics Systems Inc. as a method to decontaminate items contaminated with either radiological materials or agents. Decontamination is accomplished either by removal of particulates in the case of radiological contaminants or by solubilization in the case of agents. A schematic of the process is shown in Figure 14.

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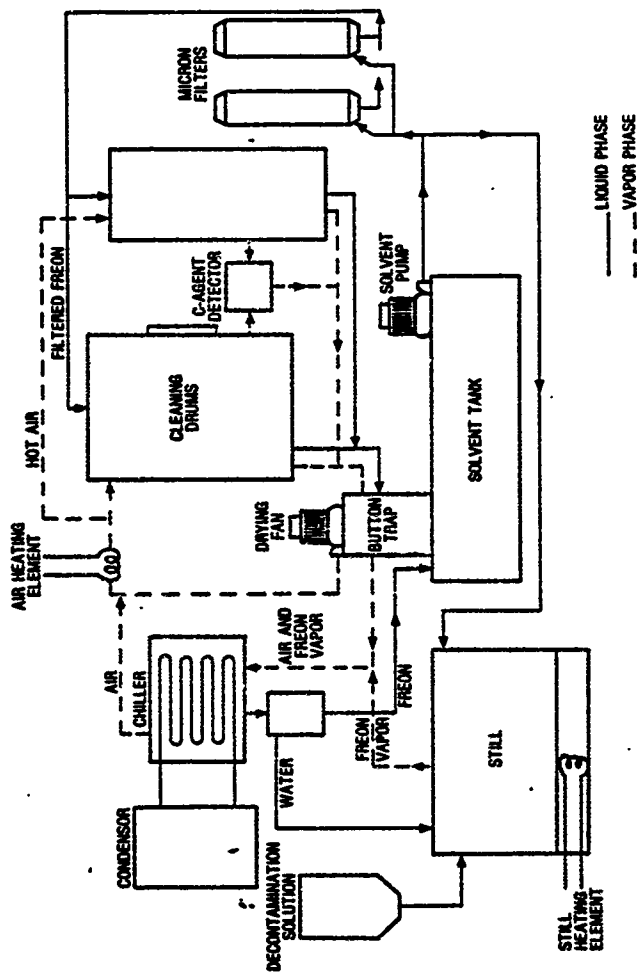
FIGURE 14. RADKLEEN PROCESS (HEALTH PHYSICS SYSTEMS INC.)

Experimental work has been performed on the capability of
RadKleen in agent removal from clothing, rubber and wabbing.* The data
indicates that over 90 percent of GD or HD can be extracted in 1 to 3
minutes by the solvent, Freon 113®, which is used in the RadKleen process.
Thus, the effectiveness of the method has been established for personal
articles in relation to agent removal. No work has yet been done in the
explosives area; however, the mode of decontamination (particulate removal
versus solubilization) may be inferred by analyzing the solubilities of
explosives in chlorinated solvents. TNT, NG and to some extent Tetryl may
be removed by solubilization with Freon 113® because of the high solubil-
ities of these explosives in chloroform and other chlorinated organics.

If explosives are removed as particulates (because of low sol-
ubility) then the method could only be considered as a surface treatment
and would be less advantageous then other methods which allow decontam-
ination of the sub-surfaces of porous materials. However if the explo-
sives is solubilized then the method has merit.

RadKleen may be applied to buildings in various ways including
spraying, volatilizing or using a spray and vacuum device. The uncer-
tainities of spraying and volatilizing Freon 113® are the length of time
required for the contaminated solution to diffuse outward from the build-
ing materials and the removal efficiency. Until the diffusional phenomena
is characterized it can only be speculated that complete decontamination
by spraying will be feasible.

A device shown in Figure 15 could be used to continuously spray
and recover Freon 113®. The solvent could then be vacuum collected with a
single nozzle. The uncertainties of this method are related to diffusion
and removal efficiency. The use of the vacuum would establish a pressure
gradient which may enhance diffusion of the contaminated solvent outward.

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* Personal communication with Ned Colburn of USATHAMA.

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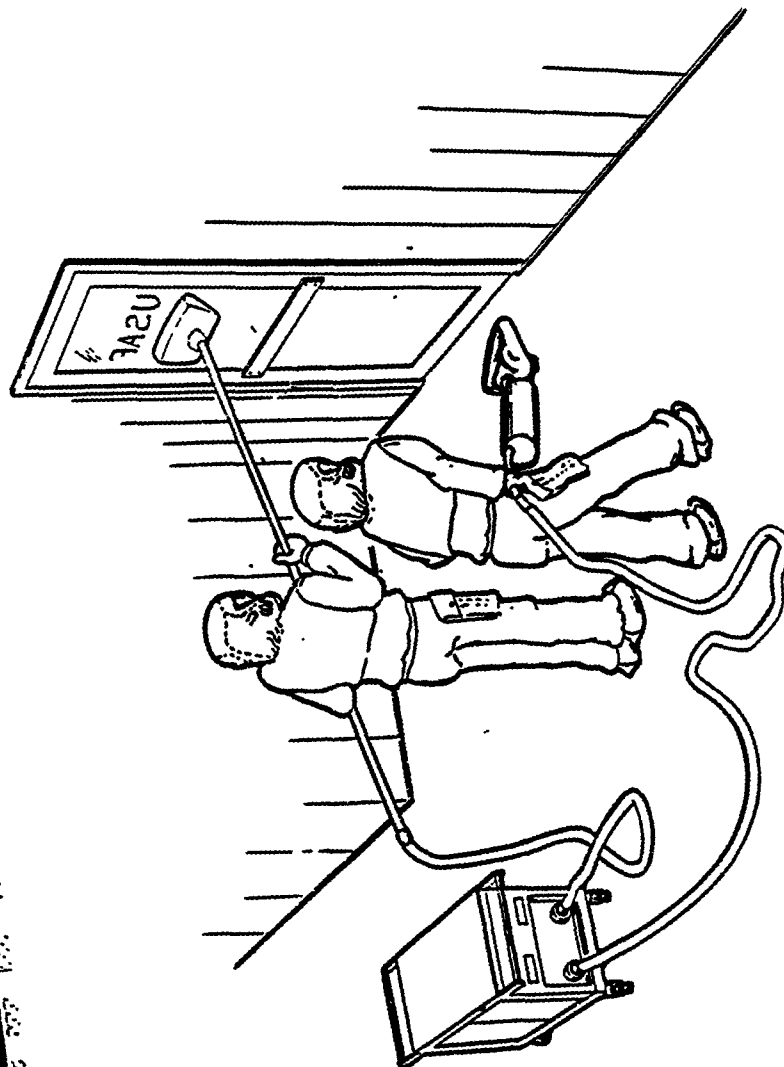
FIGURE 15. STANLEY STEAMER TYPE APPLICATION OF RADKLEEN PROCESS (HEALTH PHYSICS SYSTEMS INC.)

7.3.4.3 External Steaming

Steaming is a widely used method for removal of surface deposits of explosives. It is primarily a physical removal process where the action of the steam loosens explosive particulates from the surface. The particulates are collected intact in a sump and decomposed usually by incineration.

Other aspects of steaming may contribute to the building decontamination such as hydrolysis of the explosives (e.g. NG), solubilization (e.g., NG, NC) and thermal decomposition (e.g. NG, tetryl).

Steam cleaning with the use of an external steam generator entails pumping steam into a sealed building for several hours or days. The steam would permeate the building materials and equipment and physically remove, solubilize and/or decompose the explosive residues. The condensate would be collected in a sump and continuously removed for waste treatment. A steam generator may not be required if there are steam pipes in the building. In this case, steam could be generated from an on-site boiler and passed into the building by opening a valve and/or taking out a section of pipe. Thus, only a small pump would be required for condensate removal to a waste water treatment system.

The major disadvantage of steaming is that the physical removal of particulates would probably only occur on the surface of the building material. Thus, solubilization and decomposition of the explosive must occur in the sub-surfaces of the building material if the process is to be feasible. For all explosives other than NG and, perhaps, tetryl there would be almost no thermal decomposition of the explosives at 100 C (see Section 7.1.3). Thus, steaming should focus on the solubility of explosives in water near the boiling point to determine feasibility. Solubilities of various explosives in hot water are given in Table 24. As can be seen, even at the boiling point, most explosives have solubilities in water of less than 1 percent. An exception would be NQ which is quite soluble (9 percent) in 100 C water. Thus, a relatively large quantity of

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TABLE 24. SOLUBILITIES OF EXPLOSIVES IN HOT WATER

Explosive	Solubility in Water at 100 C (wt %)
RDX	0.28
TNT	0.0675 at 60 C
AN	Soluble
NC	Insoluble
NG	0.25 at 50 C
NQ	9.0
Lead Styphnate	Slightly Soluble
Lead Azide	0.05
2,4 DNT	0.254

water would be required to dissolve the explosives. In engineering terms this represents no major difficulties since the steam generator could be allowed to run for days if necessary without either an extensive capital or operating cost. Thus, steaming should be further considered as a decontamination method with emphasis on the explosives RDX, AN, NQ, NG and 2,4 DNT whose solubilities in water are the highest of the explosives.

7.3.5 Summary

Of the three selected extraction concepts (Steaming, Vapor circulation and Radkleen) only the Vapor Circulation concept has applicability to all explosives of interest. The Steaming and Radkleen concepts are limited because of the low solubilities of the explosives in hot water and chlorinated solvents, respectively. However, mixtures of solvents may be employed in these concepts to enhance the solubility. Thus, experimental work is required in determining optimum solvent mixtures for the Radkleen and Steaming concepts as well as specifying the solvent(s) for the Vapor Circulation concept.

At this stage, however, all three concepts will be evaluated in terms of economics.

7.4 CHEMICAL DECONTAMINATION OF EXPLOSIVES

7.4.1 Introduction

A variety of chemical methods are available which may convert explosives to non-explosive and non-hazardous products. Some of the concepts presented in this report are well documented and proven methods for explosives decontamination whereas others are more novel and will require experimental validification of their decontamination efficiency.

All candidate chemical decontamination concepts are briefly described below to introduce these concepts and present their obvious advantages and disadvantages before the concept selection process is described further. Detailed descriptions are given in Appendix III.

7.4.2 Concept Descriptions

7.4.2.1 Radical Initiated Decomposition of Explosives

The chemical generation of hydroxyl radicals with Fenton's reagent and the generation of carbon-based radicals (ketyls) is hypothesized to initiate the complete decomposition of nitroaromatic and nitramine explosives to volatile and non-toxic gases. This concept is based on the precedent that hydroxyl and carbon-based radicals which are generated either radiolytically or photochemically leads to very effective destruction of these classes of explosives.

Advantages

- Production of reactive radicals by chemical means may be performed within material matrix and allow internal explosives decomposition.

- The radical flux may be greater via chemical methods compared to radiolytic or photochemical methods.
- Chemical production of radicals requires inexpensive and safe reagents.

Disadvantages

- Explosives may have limited solubilities in Fenton's Reagent.

7.4.2.2 Base Initiated Decomposition of Explosives

Basic solutions will initiate the rapid decomposition of a wide range of explosives to non-explosive and volatile or non-toxic products.

Advantages

- Decomposition reactions are rapid at relatively low temperatures.
- Catalysts may be employed which will significantly increase the decomposition rate of a number of explosives.
- Gaseous products or low molecular weight ionic material are formed from a variety of explosives.

Disadvantages

- Relatively high pH solutions must be used.
- Explosives will have limited solubilities in aqueous solvent systems.

7.4.2.3 Decomposition of Explosives with DS2

DS2 is an a decontaminating solution for nerve agents which may have unique ability to initiate the rapid decontamination of a wide range of explosives. DS2 contains sodium hydroxide in a solvent system which has strong ability to coordinate with sodium cations and thus generate "naked" hydroxide ions in highly reactive state. This concept is a variation of the "Base Initiated Decomposition of Explosives" concept but was described and evaluated separately due to its unique potential and engineering requirements.

Advantages

- DS2 has the potential for very rapid and complete decomposition of explosives.
- Most explosives will be highly soluble in DS2.

Disadvantages

- DS2 is flammable and irritating to breath and to the skin.
- Reactivity may decrease upon absorption of atmospheric moisture.

7.4.2.4 Decomposition of Explosives with Molten Reactant Systems

This concept is another variation of "Base Initiated Decomposition of Explosives" which is described separately because of its unique decomposition potential and engineering requirements. Molten waxes containing potassium hydroxide have been demonstrated to initiate "instantaneous" decomposition of several explosives.

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<u>Advantages</u>

- Potentially instantaneous decomposition of a variety of explosives.
- Products of explosives decomposition would be contained in a solidified waxy solid which could potentially be peeled off.

<u>Disadvantage</u>

- Decontamination would be restricted to material surfaces only.
- Removal of solidified wax from irregular surfaces may be difficult.

7.4.2.5 Sulfur Based Reduction of Explosives

A variety of sulfur derived reductants are known to reduce a wide range of explosives to non-explosive and volatile or non-toxic products.

<u>Advantages</u>

- Nitrate ester explosives will be converted rapidly and quantitatively into non-explosive and non-toxic products.
- Other classes of compounds will be rapidly converted into non-explosive but potentially toxic compounds.

<u>Disadvantages</u>

- Sulfur based reductants are highly odoriferous and sulfur containing gases may be liberated requiring subsequent cleanup.

7.4.2.6 Decomposition of Explosives by Reduction With Sodium Borohydride

Sodium borohydride may be utilized to reduce RDX, HMX, and nitroguanidine to non-explosive products and to reduce TNT, DNT and Tetryl to aminoaromatics (in the presence of a cobalt catalyst in aqueous based solvent systems). Sodium borohydride may also denitrate nitrocellulose and nitroglycerine to nitrogen free products.

Advantages

● An advantage of using sodium borohydride rather than sulfide based reductants is that noxious sulfur containing gases will be liberated by the latter but not by the former reductant.

Disadvantages

● Aromatic amines produced by the reduction of nitro aromatic explosives may be toxic compounds.
● Significant amounts of cobalt salts may be required to cause significant rates of reduction of nitro aromatic explosives.

7.4.2.7 Microbial Degradation of Explosives

Explosives may be decomposed by exposing them to cultured aerobic or anaerobic microbes or enzymes produced by cultured microbes.

Advantages

● Microbes would be cultured to effectively attack targeted explosives.
● Decontamination operations would be quite safe and self-sustaining.

Disadvantages

- A large developmental effort would be required to develop an optimized strain of microbes for degradation of specific explosive.
- Nitroaromatics have not been reduced past the aromatic amine stage and no ring degradation has been observed.
- Carcinogenic nitrosoamines have been detected in the microbial degradation of RDX and nitroguanidine.

7.4.2.8 Reductive Cleavage of Explosives

Zinc dust (and possibly other metals) can be used to reductively cleave the nitro groups of RDX, HMX and nitrate esters and thereby be converted into non-explosive and possibly non-toxic products.

Advantage

- Denitration of explosives occurs rapidly at ambient temperature in organic solvents which should readily solubilize these explosives.

Disadvantages

- Reactant system is a heterogeneous system which would dictate decomposition applicability for surfaces only.

7.4.2.9 Decomposition of TNT With Reactive
Amines and Acetone or Acetonitrile

TNT in bulk quantities may be rapidly and safely converted to
non-explosive products with a variety of amines in the presence of the
specified solvents.

Advantages

- Rapid solubilization and safe chemical decomposition of TNT
  to non-explosive products is known to occur.

Disadvantages

- Non-volatile toxic products may be formed that would require
  subsequent removal or reaction.
- The solvents of choice for the reaction are flammable.

7.4.2.10 Decomposition of Explosives Using Ultraviolet
Light and Hydrogen Peroxide or Acetone

Ultraviolet irradiation of a wide range of explosives which are
dissolved in dilute aqueous solutions of hydrogen peroxide or acetone
leads to quantitative decomposition to gaseous products.

Advantages

- This concept may be a highly effective surface
  decontamination process for a variety of explosives.

Disadvantages

- Decontamination will not be feasible for explosives located within a building matrix.
- Surface decontamination will not be applicable to complex surfaces with non line-of-sight exposure to the UV lamps.

7.4.2.11 Decomposition of Explosives Using
Gamma Radiation and Water or Acetone

A variety of explosives when dissolved in water (or organic solvents) and subjected to gamma radiation readily undergo decomposition to volatile products.

Advantage

- Gamma radiation is capable of deeply penetrating all building materials.

Disadvantages

- Gamma radiation initiated decomposition of explosives which are deposited within a building material matrix would be very effective only when that explosive has been wet or dissolved by some permeating solvent.
- Reaction products may be toxic and require further removal.
- Gamma radiation usage requires a high degree of remote control equipment and significant precautions towards personnel safety.

7.4.2.12 Chromic Acid Oxidation of Explosives

RDX and HMX may be completely decomposed to gaseous products and nitrate ions. TNT, DNT and Lead Styphnate may be converted to desensitized materials.

Advantages

• Various explosives will undergo quantitative conversion either to gaseous degradation products or to desensitized compounds.

Disadvantages

• Strongly acidic solutions will probably damage concrete materials.
• Disposal of chromium containing wastes is difficult.

7.4.2.13 Reduction of Explosives With Active Metals and Acids

Various explosives will be reduced to non-explosive products upon treatment with heterogeneous systems consisting of various active metals and acid.

Advantages

• A wide range of explosives may be readily reduced to non-toxic products.

Disadvantages

- The reactant system is a heterogeneous mixture which will be restricted to surface only applications.
- Acidic reactant solutions will probably damage concrete materials.

7.4.2.14 Nucleophilic Displacement of Nitro Groups in Aromatic Explosives

All but one of the nitro groups in aromatic explosives may be readily replaced by various thiolate nucleophiles to render these explosives inert.

Advantages

- The denitration reactions proceed rapidly at room temperatures in a variety of explosives solubilizing solvents.

Disadvantages

- Reaction products will contain a residual nitro group and attached thiol ethers and may be toxic.
- The thiolate reactants and their potential coupling products will probably be odoriferous and require subsequent treatment and/or removal.

7.4.2.15 Oxidation of Explosives With Ozone

Ozone can initiate the decomposition of some explosives dissolved in aqueous solution. Ultraviolet radiation exerts a significant synergestic effect upon the rate of decomposition of various explosives.

Advantages

● Gaseous ozone may be used to decompose explosives which are
within a building material matrix.

Disadvantages

● Ozone by itself has a low effectiveness for the decomposition
of most explosives.
● The effectiveness of ozone toward explosives degradation is
greatly increased by the simultaneous application of ultra-
violet radiation but this variation limits this approach to a
surface only concept.

7.4.2.16 Reversible Reduction of DNT with Ascorbate

Most isomers of DNT upon treatment with ascorbic acid may be
readily converted to ionic species which will be readily solubilized in
water.

Advantages

● 2,5-; 3,4-; and 2,3-DNT are readily converted into their
dianions which are water soluble.

Disadvantages

● 2,4- and 2,6-DNT (which represent 98 percent of DNT isomers)
are reduced to products which are insoluble in water.
● This concept represents a selective solubilization process
rather than a decontamination process.

7.4.2.17 Solid State Hydrogenation of Explosives

Explosives may be reduced by hydrogenation with a mixture of hydrogen sulfide and carbon monoxide at elevated temperatures (with a heterogeneous catalyst) or by a two step process involving initial treatment with nickel carbonyl followed by hydrogenation with hydrogen.

Advantages

- Explosives may be reduced within a building material matrix by reacting with the gaseous reagents.
- Nickel catalyst could be deposited within the material matrix by heating the nickel carbonyl.
- Nitrate esters would be reduced to non-toxic alcohols.

Disadvantages

- Nickel carbonyl is extremely toxic and explodes readily.
- Reduction employing hydrogen sulfide and carbon monoxide could only be at high temperatures.
- Toxic reduction products (from nitroaromatic and nitramine explosives) would be left in material interior.

7.4.3 Chemical Decontamination Concept Evaluations

All candidate chemical concepts briefly described in the previous section were evaluated with respect to the two criteria of the "Critical Chemical Process Requirements" and the seven criteria of the "Preliminary Evaluation Ratings" previously described. Many concepts contained several variations and were also determined to be distinctly

more effective for one type of explosive compared to other explosives. In
these cases the concepts were scored by evaluating the best possible var-
iation with respect to the explosive which had the greatest applicability.
Two variations of the concept "Base Initiated Decomposition of Explo-
sives" were described in separate concept description forms since these
variations encompassed sufficiently different engineering requirements or
background information. These variations are "Decomposition of Explosives
With DS2" and "Decomposition of Explosives With Molten Reactant Systems"
and each was evaluated separately. The tabulated scores for each concept
are shown in Table 25 and include the summed scores for the Critical
Chemical Process Requirements and the Preliminary Evaluation Ratings and
the separate Critical Chemical Process Requirements scores. It can be
seen that the total rating scores of the surviving concepts ranged from 12
from to -2. Candidate chemical concepts 1, 2, 5, 6, 7, and 8 achieved
scores of between 12 and 10 whereas concepts 16 and 17 did not survive the
Critical Chemical Process Requirements since destruction efficiency scores
of -2 were achieved by each of these concepts.

The rating scores for the safety criteria deserve some comment.
For any chemical decontamination reagent to be significantly reactive,
that reaction must generally be somewhat exothermic. This heat liberation
could cause the temperature of the reagent system to increase signifi-
cantly which could lead to an explosion. Many warnings are listed in the
literature concerning the explosion hazards associated with the applica-
tion of concentrated reagent solutions to significant amounts of explo-
sives. To accommodate the predicted heat evolution from a variety of re-
actant systems, it is assumed that the reagent will be applied in a suf-
ficiently large volume of solvent which will serve as a heat sink to dis-
sipate the heat evolved from the decomposition reaction(s). Thus the po-
tential explosivity of various concepts was estimated by assuming that
relatively large volumes of dilute liquid reagent would be added to rel-
atively small amounts of explosives. If large pockets of explosives were
suspected or known to be present in a decontamination target site, the

TABLE 25. CHEMICAL DECONTAMINATION OF EXPLOSIVES

Criteria	Radical Initiated	Base Initiated	Sodium Borohydride	Sulfur Based Reduction	Reductive Cleavage	Microbial	DS2	Gamma Radiation	Amines and Acetone/ Acetonit.
Mass Transfer	+	++	++	++	++	+	++	++	++
Destruction Efficiency	++	++	++	++	++	+	++	++	+
Safety	+	-	+	-	-	++	-	-	-
Damage to Building	++	++	++	++	++	++	++	++	++
Penetration Depth	-	-	-	-	-	-	-	-	-
Applicability to Complex Surfaces	++	++	++	++	++	++	++	++	++
Operating Costs	++	++	++	++	++	++	++	++	++
Capital Costs	++	++	++	++	++	-	++	++	-
Waste Treatment Costs	+	+	-	+	+	++	-	-	++
Total/Pre-Screen Total	12/3	11/4	11/4	10/4	10/4	10/2	8/4	8/4	7/3

TABLE 25. CONTINUED

Criteria	UV and Acetone	Molten Reactant Systems	Chromic Acid	Active Metal and Acid	Displac. Aromatic Explosives	Ozone	Ascorbate Ion	Solid State Hydog.
Mass Transfer	++	+	+	+	++	+	++	-
Destruction Efficiency	++	++	++	+	+	+	-	-
Safety	-	-	-	-	-	-		
Damage to Building	++	+	-	-	-	-		
Penetration Depth	-	-	-	-	-	-		
Applicability to Complex Surfaces	-	++	++	++	++	-		
Operating Costs	++	-	++	+	-	-		
Capital Costs	+	++	+	++	++	+		
Waste Treatment Costs	++	++	-	+	-	+		
Total/Pre-Screen Total	7/4	6/3	4/3	4/2	2/3	-3/2	-/0	-/3

probable safest first step in the decontamination scenerio would involve
an initial inerting process such as solvent washing. The best feasible
chemical decontamination process could then be applied in a safe manner in
a secondary process.

All chemical decontamination concepts received either a -1 or -2
rating under the Penetration Depth criteria. These scores represent
either penetration depths of up to 1/8 inch or surface removal only, re-
spectively. These scores were uniformly assigned to homogeneous reactant
liquids or heterogeneous reactant liquids respectively. A +1 and +2 rat-
ing indicated penetration depths between 1/8 in and the thickness of the
building material and were reserved for gaseous or thermal treatments. A
-1 rating does not necessarily imply that liquid decontaminants would not
penetrate past 1/8 inch into the building material. The penetration depth
of homogeneous liquid reactants would be a function of residence times,
reactant viscosities and reactant temperatures. It was assumed that a 1/8
inch penetration could be achieved by a normal application of such liquid
reactants. Residence times could be increased by using gels or foams and
by applying backings to these structures.

Based on the overall scores achieved in our concept evaluations,
five chemical decontamination concepts were chosen for experimental
valididification in the Phase II studies. These decontamination concepts,
their total ranking scores, and the explosives which are potentially
applicable for decontamination by each concept are shown in Table 26.

The concept "Microbial Degradation of Explosives" was not chosen
for verification in the Phase II experimental study, even though it was
highly ranked, because significant and costly developmental studies would
be required to culture microbes which had the activities required for
effective decontamination.

The minimum number of chosen concepts which are known or pre-
dicted to be applicable for each explosive is tabulated in Table 27.

TABLE 26. SURVIVING CHEMICAL DECONTAMINATION
CONCEPTS AND POTENTIALLY APPLICABLE EXPLOSIVES

Concept	Scores	Potentially Applicable Explosives
• Radical Initiated Decomposition of Explosives	12/3	TNT, DNT, RDX, HMX, Tetryl(?), NG(?), NQ(?), NC(?)
• Base Initiated Decomposition of Explosives	11/4	TNT, DNT, RDX, HMX, NG, NQ, NC, Tetryl(?)
• Sulfur Based Reduction of Explosives	10/4	TNT, Tetryl, RDX, HMX, NG, NQ NC, DNT(?)
• Decomposition of Explosives by Reduction With Sodium Borohydride	11/4	TNT, DNT, RDX, HMX, NG, NC, NQ(?), Tetryl(?)
• Reductive Cleavage of Explosives	10/4	RDX, HMX(?), NQ(?), TNT(?), DNT(?), Tetryl(?), NG(?), NC(?)

TABLE 27.   NUMBER OF APPLICABLE CHOSEN CONCEPTS FOR EACH EXPLOSIVE

Explosive	Minimum Predicted Number of Applicable Concepts
TNT	4
DNT	3
Tetryl	1
RDX	5
HMX	4
NG	3
NC	3
NQ	2

Detailed description forms of all of the chemical decontamination concepts are found in Appendix III. Each of the five surviving decontamination concepts are also described in some detail in the following section. These descriptions are divided into three sections: General Descriptions, Criteria Evaluation Highlights, and Applicable Explosives. The General Description section discusses the background information or data which relates to the probable efficacy of the concept. The Criteria Evaluation Highlights section explains the rationale behind the rating scores of some of the criteria. The Applicable Explosives section indicates those explosives which are known or predicted to be decomposed by the concepts.

7.4.4   Descriptions of Most Promising Chemical Decontamination Concepts

7.4.4.1   Radical Initiated Decomposition of Explosives

7.4.4.1.1   General Description

This concept involves the decomposition of explosives by hydroxyl radicals (or carbon-based radicals) which are generated chemically rather than from either ultraviolet photolysis or gamma radiolysis.

The rationale and precedents contributing to this concept are based on results achieved from the decomposition of explosives through ultraviolet photolysis and gamma radiolysis methods and other data which are described below. Recent patented research (Andrews, 1976; Andrews, 1977) has shown that the ultraviolet photolysis of aqueous solutions of TNT, DNT, RDX and HMX containing small amounts of either acetone or hydrogen peroxide leads to nearly complete explosives decomposition within relatively short periods of time. For illustration, ultraviolet photolysis of an aqueous solution of TNT (100 ppm) containing one percent acetone for three hours led to complete TNT decomposition and the products were carbon dioxide, ammonia and a trace amount of cyanide. Labelling studies indicated that the carbon dioxide carbon atoms originated from cleavage of the aromatic ring of TNT. The decomposition of explosives was shown to be slower when hydrogen peroxide rather than acetone was used as the additive.

The initial postulated steps in the photolytic initiated decomposition of these explosives is the formation of methyl or hydroxyl radicals from acetone or hydrogen peroxide respectively. (In each case, these photochemical reactions are well known processes). These radicals are then postulated to abstract active hydrogen atoms from the explosives to generate unstable explosives intermediates which are then suggested to decompose to ammonia and carbon dioxide when subjected to continued pho-

tolysis. However the need for continued photolysis in the further decom-
position of these explosives intermediates has not been demonstrated. If
continued ultraviolet photolysis of the explosives intermediates is not
required for continued decomposition, then hydroxyl or carbon-centered
radicals which are generated chemically should have identical reactivities
in decomposing explosives as the Ultraviolet Radiation/Hydrogen Acetone/-
Peroxide reactant system. The hypothesis that hydroxyl (and other) radi-
cals alone can initiate the decomposition of explosives is supported by
information concerning the gamma irradiation of various explosives. It is
known that dry TNT in the solid state undergoes very little physical and
chemical change when exposed with doses in the order of 20 megaRoentgens
of gamma radiation (Piazzi, 1965). However, aqueous slurries of TNT are
reduced in concentration by approximately 30 percent at a dose level of
only 4.1 megarad (Wentsel, 1981). TNT levels in pink water were also re-
ported to be reduced by gamma irradiation from 89 mg/l to 2 µg/l but no
radiation dose was given (Wentsel, 1981). It is also well known that
gamma irradiation of water readily produces hydroxyl radicals (Appleby,
1969; Burns, 1981; Allen, 1953). Therefore it may be presumed that the
effectiveness of gamma radiation towards the decomposition of TNT and
other explosives in aqueous solutions may be primarily due to the attack
of hydroxyl radicals on these explosives.

The Radical Initiated Decomposition of Explosives concept is
based on the chemical generation of hydroxyl and carbon-centered radicals
which are predicted to initiate the decomposition of a variety of explo-
sives in various building materials. Hydroxyl radicals may be readily
generated at ambient temperatures by Fenton's Reagent which consists of a
homogeneous solution of ferrous salts in concentrated aqueous hydrogen
peroxide at relatively low pH (Walling, 1974). Hydroxyl radicals gen-
erated from Fenton's Reagent have been shown to have similar relative re-
activities towards a number of substrates as those generated in the gamma
irradiation of water (Walling, 1973) which suggests that the efficiency of
explosives decomposition may be similar to that achieved with "wet" gamma

irradiation. It is also possible that a greater flux of hydroxyl radicals will be generated in Fenton's Reagent compared to either the gamma irradiation or the Ultraviolet Radiation/Hydrogen Peroxide/Acetone systems which are known to effectively initiate the decomposition of a variety of explosives. It is also feasible to generate methyl radicals, which are indicated to be more reactive than hydroxyl radicals (Andrews, 1976), from Fenton's Reagent by employing DMSO as a cosolvent (Walling, 1974). Alternate methods also exist to chemically generate a variety of potentially active radicals (Bernardi, 1973). One of the main advantages of using this concept over the Ultraviolet Radiation/Hydrogen Peroxide/ Acetone reactant system for building decontamination is that homogeneous chemical reagent systems may penetrate into the building material matrix and effect internal decontamination which is not possible with photolytic processes.

A variation of this concept involves the generation of carbon-based radical species such as "ketyls" which may possibly have similar explosives decontamination effectiveness as methyl intermediates which are usually generated by reacting alkalai metals (which are highly flammable) with various ketones. However, a recent report indicates that potassium (a very reactive alkalai metal) may be safely deactivated by adsorption on silica gel (Levy, 1981). This adsorbed form of potassium readily produces a blue color at room temperature when in the presence of ketones which is indicative of ketyl formation. Silica gel would have another beneficial effect by facilitating the adsorption of the deposited explosives into the silica gel-potassium reactant matrix. If ketyls react in the same manner as methyl radicals, decomposition of explosives via the generation of these reactive intermediates may readily occur. However, this reactant system would be limited to the decontamination of surfaces only since potassium adsorbed silica gel would be applied as a slurry which could not penetrate the surface.

These reactions are shown below:

• Fenton's Reagent

$$H_2O_2 + Fe^{+2} \longrightarrow Fe^{+3} + OH^- + \dot{O}H$$

$$\dot{O}H + RDX, HMX, TNT, DNT \longrightarrow \text{Unstable Intermediates} \longrightarrow \text{Small, Gaseous Compounds}$$

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- Ketyl Formation

Potassium (on silica gel) + $R_2CO \rightarrow R\text{-}\overset{\overset{O^-}{|}}{C}\text{-}R$ (Ketyl)
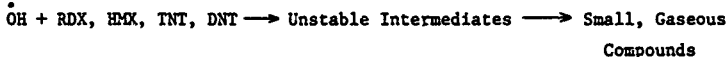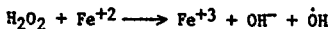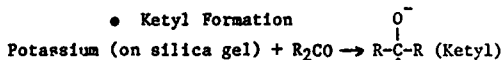
Ketyl + RDX, HMX, TNT, HMX $\longrightarrow$ Unstable Intermediates $\longrightarrow$ Small, Gaseous Compounds

7.4.4.2.1 Criteria Evaluation Highlights

The Radical Initiated Decomposition of Explosives concept was evaluated in terms of the merits of Fenton's Reagent rather than the ketyl system. The former rated better than the latter in Mass Transfer, Destruction Efficiency, Safety, Penetration Depth, Operating Costs, Capital Costs, and Waste Treatment Costs. The use of organic cosolvents, surfactants, or complexing agents to solubilize explosives in the aqueous Fenton's Reagent was assumed in evaluating this concept.

7.4.4.1.3 Applicable Explosives

The Ultraviolet Radiation/Hydrogen Peroxide/Acetone concept is applicable to nitroaromatic (TNT, DNT) and nitramine (RDX, HMX) explosives. Therefore hydroxyl or carbon-based radicals generated chemically are predicted to be applicable not only to these explosives but possibly also to Tetryl (a nitroaromatic) and NQ (a nitramine). The use of organic cosolvents or surfactants in Fenton's reaction would allow the effective dissolution of most explosives to allow their chemical reaction.

7.4.4.2 Base Initiated Decomposition of Explosives

7.4.4.2.1 General Description

A large variety of explosives are known to be effectively decomposed when treated with basic solutions: RDX, HMX (Croce, 1979); DNT

(Clear, 1945; Beck, 1978); Nitrocellulose (Dogliotti, 1974; Clear, 1945; Ottinger, 1973), nitroguanidine (Okamoto, 1978; Smith 1982) and lead azide (Clear, 1945). The literature is not complete concerning TNT but the available data does suggest that TNT may be decomposed under basic conditions since nitrite ion has been detected under these conditions (Hammersley, 1975). RDX, HMX, NG, NC and NQ are known to decompose to volatile gases and/or low molecular weight and non-toxic products (See Concept Description Form in Appendix III). TNT and DNT are presumed to undergo nitro group displacement by hydroxide ion to give mixtures of non-explosive nitrophenols. These reactions are shown below:

$$RDX, HMX \xrightarrow{OH^-} CH_2O, N_2O, NH_3, N_2, HCO_2^-$$

$$NG \xrightarrow{OH^-} CH_2CO_2^-, HCO_2^-, NO_3^-, NO_2^-$$

$$NC \xrightarrow{OH^-} org. \ acids, NO_3, NO_2, NO_x, CO_x, cyanides$$

$$NQ \xrightarrow{OH^-} N_2O, CO_2, NH_3$$

$$ArNO_2 \ (TNT, DNT) \xrightarrow{OH^-} ArOH$$

$$Pb(N_3)_2 \xrightarrow{OH^-} Pb(OH)_2 + N_3^-$$
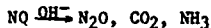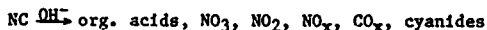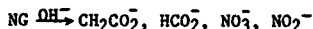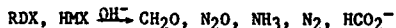
The reaction rates of these decomposition reactions are in general of such magnitude that effective decontamination of a variety of explosives may be achieved in relatively short times under conditions which are described below: RDX has been estimated (by Battelle) to undergo 99.9 percent decomposition in aqueous solutions containing micellar catalysts at pH 10 and 75 C in approximately 1.3 hours (Croce, 1979). A nitrocellulose dispersion (5 percent) containing five percent sodium hydroxide underwent complete decomposition at 60 C in 0.23 minutes (Kenyon, 1936). Also, a two percent solution of DNT in a four percent solution of sodium

hydroxide in 75 percent aqueous ethanol led to assumed complete decomposition at 45 C within approximately 15 minutes after addition of the DNT (Clear, 1945).

The basic hydrolysis rates of RDX, HMX, and NC have been reported to increase significantly in the presence of long chain quaternary ammonium halide type surfactants (Croce, 1979; Okamoto, 1979). These increased rates are attributed to a micellar catalytic affect but also may be caused by potential solubilization of these explosives by these surfactants. These long chain quaternary surfactants are also known to cause precipitation of the TNT Janovsky complex which is formed under basic conditions (Okamoto, 1979) which precludes the use of these specific surfactants with TNT. However it is quite feasible that suitable quaternary ammonium (or other) surfactants can be employed which will help to solubilize TNT and other nitroaromatic explosives and also catalyze the basic initiated denitration of these explosives.

One interesting variation of Base Initiated Decomposition of Explosives involves the application of a molten (80-100 C) waxy carrier containing potassium hydroxide as the decontaminant. This system has been reported to initiate "instantaneous" decomposition of RDX and pentaerythritol tetranitrate (Pytlewski, 1979). A separate description form is included in this report entitled Decomposition of Explosives With Molten Reactant Systems which describes this concept.

Another variation in the basic decomposition of explosives involves the use of a DS2, a reactant system currently used to decontaminate nerve agents. DS2 (a solution of 70% diethylenetriamine, 28% ethylene glycol monomethyl ether and 2% sodium hydroxide) contains the "superbasic" hydroxide ion as a result of the lack of complexation of the hydroxide by sodium cation. The high basicity and expected high solvating power of DS2 should make it extremely applicable for the decomposition of a variety of explosives. The same reaction products should be generated in DS2 as in aqueous basic reagents but the reaction rates are expected to be significantly higher in DS2. The relatively low viscosity and surface tension of

this system would probably allow an increased degree of diffusion into the building matrix which would lead to enhanced internal decomposition of explosives. A significant problem involved in the use of DS2 is its high flammability which may however be effectively controlled by spraying on as a gel or foam. A separate description form entitled "Decomposition of Explosives With DS2" describes this concept.

Another variation in the hydroxide ion initiated nucleophilic displacement of nitro functions of aromatic explosives (TNT, DNT and Tetryl) is the use of thiolates as the reactive basic (nucleophilic) reagents (Benedetti, 1982; Cogolli, 1979). Thiolate ions are significantly more reactive than hydroxide ion and may displace nitro functions in aromatic explosives much more rapidly than hydroxide ion. A separate description form entitled "Nucleophilic Displacement of Nitro Group in Aromatic Explosives" describes this concept.

7.4.4.2.2 Criteria Evaluation Highlights

This concept was evaluated in terms of the merits of aqueous basic solutions rather than any variation. The use of organic cosolvents, surfactants, or complexing agents to solubilize explosives was assumed in evaluating this concept. This concept received a -1 rating in Safety due to the eye and breathing hazards involved in spraying caustic solutions. This concept scored high in Mass Transfer, Destruction Efficiency, Damage to Building, Applicability to Complex Surfaces, Operating Costs and Capital Costs.

7.4.4.2.3 Applicable Explosives

Firm documentation indicates that RDX, HMX, nitroglycerine, and nitrocellulose are effectively decomposed in basic solutions. However, decomposition of nitroguanidine under basic conditions is indicated by one study (Okamoto, 1978) but another study indicates that nitroguanidine does

not decompose in basic solutions (Smith, 1982). A Standard Operating
Procedure for the decontamination of waste DNT involves treatment with
aqueous ethanolic sodium hydroxide (Clear, 1945). The products were not
specified but presumably nitrophenols were formed through nitro group
displacement by hydroxide ion (Beck, 1978). TNT and Tetryl would be pre-
dicted to be more susceptible to nucleophilic attack by hydroxide than DNT
and are therefore presumed to be denitrated by basic treatment also.

7.4.4.3 Sulfur Based Reduction of Explosives

7.4.4.3.1 General Description

A large variety of explosives may be effectively reduced by em-
ploying sulfide, hydrosulfide, or sulfite reducing agents. Nitroglycerine
and nitrocellulose yield glycerine and cellulose respectively as well as
volatile gases (Urbanski, 1964) On the other hand, TNT and presumably
Tetryl and DNT give aromatic amines which may be presumed to be toxic,
when reduced with these reagents (Kaye, 1980; Clear, 1945; Urbanski, 1964;
Army Tech. Manual Military Explosives). RDX, HMX and nitroguanidine are
also known to readily react with these reducing reagents to presumably
yield hydrazine (hydrazide, in the case of nitroguanidine) derivatives
(Private Communication). These reactions are shown below:
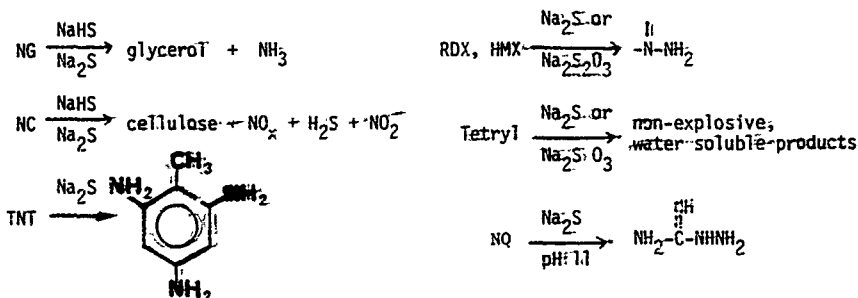
These reduction rates in general are quite rapid even at room temperatures under a variety of conditions which are illustrated below. An 8% aqueous dispersion of nitroglycerine containing 15% sodium sulfide hydrate at room temperature was completely decomposed in several hours (Clear, 1945). Caution must be exercised when decontaminating nitroglycerine by this procedure due to the potentially dangerous temperature increase generated by this reaction (Ottinger, 1973). A 0.6% solution of nitrocellulose in a water/ethanol solution (40:60) containing 4% potassium hydrosulfide achieved 99% reduction in 4 hours at 20 C (Rassow, 1924). A 0.01% aqueous solution of nitroguanidine at pH 11 containing 0.1% sodium sulfide achieved complete decomposition in approximately 32 hours (Smith, 1982).

The odoriferous nature of the sulfur containing reductants and their reaction products requires that secondary treatment(s) will probably be necessary to reduce the level of these compounds to an acceptable level after decontamination of the building has been performed. Potential reagents for this secondary treatment are hydrogen peroxide and percarboxylic acids.

7.4.4.3.2 Criteria Evaluation Highlights

This concept received a -1 rating in Safety due to the danger inherent in spraying sulfur based reagents at elevated pH's. However, this concept scored high in Mass Transfer, destruction Efficiency, Applicability to Complex Surfaces and Capital Costs. Operating And Waste Treatment were given +1 ratings because of the need to remove or convert sulfur based reagents or by products and to dispose of sulfur containing waste products.

7.4.4.3.3 Applicable Explosives

Nitroglycerine, nitrocellulose, nitroguanidine, TNT, Tetryl, RDX and HMX are known to undergo decomposition with these reductant systems. However the products formed from nitroguanidine, Tetryl, RDX and HMX have not been specified. Furthermore, the reduction efficiency of RDX and HMX is not known with certainty since this information was verbally acquired from an employee of an explosives processing company.

7.4.4.4 Decomposition Of explosives by Reduction With Sodium Borohydride

7.4.4.4.1 General Description

Sodium borohydride is a "clean" reducing agent in comparison to sulfur based reductants, and has similar reductive power and scope of applicable explosives as the sulfur based reductants. Thus secondary treatments would not be necessary with this reagent, as is the case with sulfur based reductants, to remove noxious compounds. However, reductions with sulfur based reductants has been documented with a wider range of explosives than sodium borohydride. Sodium borohydride may be used in aqueous solution but will slowly decompose with the evolution of hydrogen. One negative aspect in the use of sodium borohydride for reducing aromatic explosives is that cobalt (Co^{+3}) salts must be employed as catalysts to accomplish nitro group reduction (Vlcek, 1961). DNT was reported to given aromatic amines or hydroxylamines with this reductant system. The disposal of these cobalt salts may require specific disposal requirements.

The decomposition times and reaction conditions of a number of reductions are described below. RDX solutions (1 percent) in various organic solvents have been completely reduced by sodium borohydride to give

hydrazine derivatives (presumed) in 24 hours at 38 C (Tulis, 1977).
Quantitative denitration of nitrocellulose in acetone solutions was
achieved in an unspecified time period (Masuelli, 1954). Complete
reduction of 2,4-DNT was achieved within 10-30 minutes in aqueous solutions
at room temperature with DNT/Cobalt Catalyst molar ratios of 10:1 (Vlcek,
1961).

7.4.4.4.2 Criteria Evaluation Highlights

The use of organic cosolvents, surfactants or complexing agents
to solubilize explosives was assumed in evaluating this concept. This
concept received a +1 rating in Safety due to the minimum hazards involved
in handling aqueous or organic solutions of sodium borohydride. This
concept scored high in Mass Transfer, Destruction Efficiency, Damage to
Building, Applicability to Complex Surfaces, Operating costs and Capital
Costs. A -1 score was achieved in the Waste Treatment Costs criterion
since incineration or Hazardous Landfills was assumed to be necessary to
accommodate the disposal of cobalt.

7.4.4.4.3 Applicable Explosives

Examples of nitramines (RDX), nitroaromatics (DNT), and nitrate
esters (NC) explosives have been shown to undergo decomposition with sod-
ium borohydride. Thus it is possible that other explosives of these types
may also be decomposed with sodium borohydride. Nitramines may be ex-
pected to give hydrazines, nitroaromatics will give potentially toxic
aromatic amines, and nitrate esters to known to be denitrated to alcohols.

7.4.4.5 Reductive Cleavage of Explosives

7.4.4.5.1 General Description

A recently developed analytical method for the detection of microgram quantities of RDX and pentaerythritol tetranitrate (PETN) utilizes the reaction of these explosives with a suspension of zinc dust in an aromatic solvent (Wyant, 1977). This reaction functions by displacing nitrite ions from the explosives which are subsequently detected by a spot test. Such a displacement reaction would serve to decontaminate all explosives which were prone to such reductive cleavage reactions. This reaction occurs rapidly at room temperature (rate data is not available) and presumable in organic solvents which will readily dissolve and promote the reaction of a variety of explosives.

This heterogeneous reaction system would be applicable only to surface decontamination due to the predicted lack or migration of zinc into the building material matrix.

7.4.4.5.2 Criteria Evaluation Highlights

This concept received a +2 in Mass Transfer since the organic solvents should readily dissolve a variety of explosives. The maintenance of a uniform zinc slurry on a vertical surface could be a problem which could be alleviated by the use of a gel. A score of -2 was achieved in the Penetration Depth criteria since this concept is a surface only decontamination procedure. A score of -1 was achieved in the Safety criteria since a breathing mask would probably be required when dispensing specific organic solvents. High scores were achieved in applicability to Complex Surfaces, Operating Costs and Capital costs.

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7.4.4.5.3 Applicable Explosives

The available literature (Wyant, 1977) indicates that this re-
action is applicable to RDX (a nitramine) and PETN (a nitrate ester).
Therefore, this concept is presumed to be applicable to other nitramines
such as HMX and nitroguanidine and nitrate esters such as nitroglycerine
and possibly nitrocellulose (de-polymerization must first occur before
decomposition could proceed). The applicability of this reaction to
nitroaromatics such as TNT, DNT and Tetryl is not known and thus would
require experimental validification.

7.4.5 Description of Less Promising Chemical Concepts

Those concepts with total rating scores of 8 or less were not
recommended for experimental verification at this time. A number of these
less promising chemical concepts ranked high in Mass Transfer and De-
struction efficiency but had specific applicabilities to only one or sev-
eral explosives. The most important advantages and disadvantages of these
concepts have already been presented. Overviews of these concepts are
presented in the following descriptions and some explanations of the rat-
ing scores achieved are presented. Special notice are made of those con-
cepts that are adaptable to situations other than those found in building
decontamination such as the safe decontamination of bulk explosives.

7.4.5.1 Microbial Degradation

This concept received an overall ranking of 10 but received only
a +1 in both the Mass Transfer and Destruction Efficiency criteria. Var-
ious microbes or their enzymes have been shown to reduce a variety of ex-
plosives to various products. However a serious drawback of this approach
is that microbes, in general, give incompletely reduced or toxic products.
For example, nitroaromatic explosives (to our knowledge) have not been
reduced past the aromatic amine stage by some microbes. Carcinogenic

nitroso compounds have also been detected in the microbial degradation of RDX and nitroguanidine. This approach would probably require significant research before a viable microbial method could be developed which would give efficient explosives decontamination.

7.4.5.2 Decomposition of Explosives Using
Gamma Radiation and Water or Acetone

This concept received a +8 overall ranking and a +2 ranking in both the Mass Transfer and Destruction Efficiency criteria. Gamma irradiation of dry TNT and RDX leads to relatively low degrees of decomposition at moderately high radiation dosages (Piazzi, 1965). However, gamma irradiation of these explosives in aqueous solutions or wet sediment may lead to nearly complete explosive decomposition of these explosives (Wentsel, 1981). Since it is well known that gamma irradiation of water produces hydroxyl radicals (Appleby, 1969; Burns, 1981; Allen, 1953), it may be presumed that the effectiveness of TNT and RDX decomposition in aqueous solution by gamma radiation may be partially due to the initial attack of hydroxyl radicals on these explosives. This hypothesis is reinforced by the fact that TNT and RDX in aqueous hydrogen peroxide or acetone undergo rapid decomposition when exposed to ultraviolet radiation (Andrews, 1976) since hydrogen peroxide and acetone are known to generate hydroxyl and methyl radicals respectively under these conditions. Therefore gamma radiation, coupled with water or acetone, represents a convenient source of reactive radicals which may be able to initiate decompositions of a variety of explosives within building materials due to the high penetrating power of the gamma radiation. However, this concept involving gamma radiation was not chosen for Phase Two evaluation because the chemical generation of hydroxyl radicals and subsequent presumed decomposition of explosives may be effected in a safer and less expensive manner. Furthermore the high penetration capacity of gamma radiation would not be fully utilized since the effective depth of penetration would be limited

by the penetration depth of the additives (water, hydrogen peroxide or acetone)
which may be required for effective decontamination.

7.4.5.3 Decomposition of Explosives Using Ultraviolet
Light and Hydrogen Peroxide or Acetone

This concept received a +7 overall ranking and a +2 ranking in
both the Mass Transfer and Destruction Efficiency criteria. This concept
is based on a patented process which indicates that aqueous solutions of
RDX, HMX, TNT and DNT containing either hydrogen peroxide or acetone are
decomposed by ultraviolet irradiation (Andrews, 1976). This process sup-
posedly involves the generation of hydroxyl or methyl radicals which are
the reactive species involved in the decomposition of the explosives.
These hypothesized pathways represent the basis for the concept Radical
Initiated Decomposition of Explosives which involves the chemical forma-
tion of either hydroxyl or carbon based radicals which is recommended for
Phase Two testing. The same chemistry is presumed to be operative in both
concepts. However, the concept based on ultraviolet radiation would apply
only to decontamination of surfaces which were in the line of sight of the
ultraviolet lamp and which had been pretreated with hydrogen peroxide or
acetone. By comparison, the concept Radical Initiated Decomposition of
Explosives will involve the chemical generation of hydroxyl and methyl
radicals either within a building material's matrix or on the material
surface. Therefore this latter concept was chosen for Phase Two testing.

7.4.5.4 Decomposition of TNT With Reactive
Amines and Acetone or Acetonitrile

This concept received a +7 overall ranking, a +2 rating in Mass
Transfer and a +1 ranking in Destruction Efficiency because it was sus-
pected that the reaction products from TNT were toxic. This approach has

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been used very effectively for the safe and complete decontamination of cast TNT in amounts ranging from 2g to 10 pounds within a 30 minute reaction period (Heberlein, 1976; Keith, 1974). The nature of the reaction products from TNT have not been determined but may parallel those obtained from the reaction of trinitrobenzene with diethylamine and acetone which gives a variety of nitrated aromatic and aliphatic nitro compounds (Strause, 1970). This concept received a -2 score in the Safety criteria since the reactive amine (isopropylamine) and alternate coreactants (acetone or acetonitrile) which have been previously studied are all highly flammable. It is possible that less flammable reactants of approximate equal reactivities may be employed. The reaction of TNT with reactive amines alone and with amine, water mixtures has also been shown to induce decomposition of TNT by a hypergolic reaction (Tulis, 1974) in which total destruction of TNT was claimed.

The applicability of this approach to other explosives has not been reported although a brief reference in the literature indicated that the solubility of RDX relative to TNT is not as high as desired for effective decomposition. A thorough study of the applicability of this effective TNT decontaminating concept towards a range of explosives may be warranted. Only after the reaction effectiveness and nature of products from all explosives (as well as TNT) have been determined, may the applicability of this approach toward building decontamination be judged.

7.4.5.5 Chromic Acid Oxidation of Explosives

This concept received a +4 overall ranking and a +2 rating in the Mass Transfer criteria and a +2 rating in the Destruction Efficiency criteria. This concept has been reported to be very effective for the total decomposition of RDX and HMX into volatile gases (Jurecek, 1972). The conditions for this decontamination of RDX and HMX were not reported. This concept ranked low in the Damage to Building criteria (-1) due to the expected etching and erosion of concrete and the potential damage to

electrical systems. This concept also ranked low in the Waste Treatment Cost criteria due to the costs involved in disposal of chromium in various oxidation states.

This concept could have direct applicability towards the decontamination of bulk quantities of RDX and HMX. The nitramine nitroguanidine may also be a candidate for decontamination by this concept. The oxidation of TNT and DNT to nitrocarboxylic acids is also effected by chromic acid (Kaye, 1980). However these nirocarboyxlic acid may be toxic even though they presumably have a lowered explosivity. Lead styphanate will form a precipitate of lead chromate (and a solution of styphnic acid) which effectively deactivates this primary explosive (US Army, 1971).

7.4.5.6 Reduction of Explosives
With Active Metals and Acid

This concept received a +2 overall score and a -1 Mass Transfer rating and a +1 Destruction Efficiency rating. This concept involves the addition of active metals dusts (zinc, tin or iron) to a material surface followed by application of an acid such as hydrochloric acid. Therefore this reaction involves a heterogeneous system which would have a minimal effective penetration depth. The reaction usually requires the control of an exotherm (in the case of nitroaromatics) and is then usually followed by a heating period. This concept ranked low in the Damage to Building criteria (-1) due to the nigh acidity of the reaction system.

TNT is known to react with tin and hydrochloric acid to form 2,4,6-triaminatoluene (Kaye, 1980). Since this product is an aromatic amine, it is probably toxic. DNT is probably reduced to the corresponding diaminotoluene by this reagent system. These acid initiated reductions may be feasible with various nitramines and nitrate esters. However the reduction of nitroaromatics, nitramines and nitrate esters may be more readily performed with sulfur based reductants or sodium borohydride in homogeneous and neutral or basic reaction systems at room temperatures.

7.4.5.7 Oxidation Of Explosives With Ozone

This concept received a −3 overall score and +1 score in both the Mass Transfer and Destruction Efficiency criteria. Ozone by itself has a marginal effect on the decomposition of RDX, HMX and TNT (Smetana, 1977; Roth, 1979). The preferred process for performing this concept would involve filling a room (building), which had been saturated with an explosives solubilizing solvent, with gaseous ozone and applying UV radiation. This process would lead only to surface decontamination only. This approach achieved a poor rating in the Safety, Damage to Building, Penetration Depth, Applicability to Complex Surfaces and Operating Costs criteria primarily because of the high toxicity and corrosiveness of ozone.

7.4.5.8 Reversible Reduction of DNT's With Ascorbate

This concept received a −2 rating in the Destruction Efficiency criteria and therefore failed to pass the Critical Chemical Process Requirements. This rating was achieved because this concept was applicable to all DNT isomers except 2,4− and 2,6−DNT which constitute 98 percent of commercial DNT.

7.4.5.9 Solid State Hydrogenation of Explosives

This concept received a −2 in the Destruction Efficiency criteria and therefore failed to pass the Critical Chemical Process Requirements. This concept involved the initial deposition of nickel (a hydrogenation catalyst) in the interior matrix of a building material by first saturating the material with nickel carbonyl and then heating the material to deposit the nickel. Then hydrogen, or a mixture of carbon monoxide and hydrogen sulfide (Ratcliff, 1980), would be employed to reduce various explosives in situ. The −2 Destruction Efficiency rating was assigned

because the nickel film was expected to cover the explosives which would thereby prevent their contact with the reductant gas. This concept was not ranked under the full preliminary ranking procedure but would have received very low ratings under Safety, Operating Costs and Capital Costs due to the high toxicities and explosivities of nickel carbonyl, carbon monoxide and hydrogen sulfide as well as the explosivity of hydrogen gas.

7.4.6 Combination Chemical Concepts

Several chemical concepts were developed which would have utility only coupled with either thermolysis, solvent extraction, or decomposition procedures. These chemical concepts, which are termed combination concepts, are briefly described below. Complete description forms of these concepts are contained in Appendix III.

7.4.6.1 Deactivation Of Explosives During
Thermolysis by Radical Trapping

The initial reaction steps in the detonation sequence and also during the thermolysis of explosives involve the formation of various radicals. It is proposed that sensitive explosives such as nitroglycerine may be soaked with appropriate radical traps which will intercept various propogating radicals formed during the thermolysis of these explosives. The presence of these radical trapping agents may allow the safe thermolysis of thermally sensitive explosive compounds.

7.4.6.2 Solubilization and Inerting of
Explosives Through Complex Formation

A significant problem in the chemical decomposition of most explosives is that the explosives have limited solubilities in aqueous solutions. Four of the five decontamination methods recommended for Phase

II experimental verification used water as the preferred or common solvent. Explosives are known to form a variety of stable and isolatable complexes with various complexing agents. If highly water soluble complexing agents are utilized, aqueous solubilities of explosives should be significantly increased by complex formation. The solubilized explosive complex could then be readily removed by washing or continued extraction or decomposed by a variety of decontamination agents. Complexing agents may also be used with organic solvents to enhance the solubilities of explosives in these solvents. It is also feasible that an explosive complex will have an inherently diminished explosivity compared to that explosive itself.

7.4.6.3 Formation of Water Soluble Derivatives
of Explosives Which Have Limited Water Solubility

Derivitization reactions may be employed to convert water insoluble explosives (specifically TNT or DNT) to a variety of water soluble derivatives which will permit their physical extraction or decontamination in solution. These derivitization reactions may be performed either in organic or aqueous solvents systems which could contain reagents to decontaminate the solubilized derivatives.

7.4.7 Combination Concepts Evaluations

Each of these three Combination Chemical Concepts were examined by the evaluation committee and each concept was judged to have a high potential for achieving the concept objective. These concepts were not judged in terms of the criteria used previously for decontamination since explosives decontamination was not the focus of these concepts. We recommend that the Radical Trapping and Complex-Solubilization concepts be experimentally verified in the Phase II studies for building decontamination. The derivitization concept was not chosen because the overall decontamination scenerio would involve a two stage rather than a one stage decontamination operation. Both the Complex-Solubilization and the Water Soluble Derivatives concepts could be applicable to other explosives decontamination targets such as explosives filled lagoons.

7.4.8   Chemical Applications Methods

7.4.8.1   Painting Methods

Liquid spraying is the most versatile and rapid of the application schemes. A discharge stream of liquid droplets from a nozzle or atomizer wets the surface with liquid decontamination solutions or solvents. Spraying would allow the decontaminating solution to rapidly cover simple and complex although the coverage may not be uniform. The ability of the liquid to penetrate into porous and rough surfaces depends on the viscosity and surface tension of the applied liquid. The penetration of the liquid may be improved with a high velocity spray.

Spraying is a relatively safe operation except when executed under high pressure. High pressure spraying is anticipated to cause minimal damage to building materials. Spraying utilizes low cost, readily available equipment which is very reliable and easy to maintain.

Brush and roller painting are techniques which have relatively low applicability for the application of decontamination solutions because of the manual nature of these techniques.

7.4.8.2   Wetting Methods

The hose application method is essentially a low-pressure spray system. For this reason, it also has all the advantages and disadvantages of the spraying technique, however, the equipment is less expensive than spraying equipment.

The continuous liquid flow technique is dependent on the liquid coming out of a perforated hose or pipe placed at the top of the surface. The liquid would run down the structure and react with the contaminants. The pipe or hose would be mounted on the structure and the liquid would be applied by remote control.

Very rapid coverage would be obtained using this approach with a
minimal labor effort. The liquid may not cover all the surface, espec-
ially in the porous and rough areas. Also, application in intricate areas
can be cumbersome. This method is not applicable to ceilings or other
elevated horizontal structures (pipes, beams).

The flooding application technique requires filling up the
structure with the reactive liquid, letting the liquid react, and then
draining it for waste treatment and disposal. Complete wetting of the
surface would be obtained with this technique and some subsurface decon-
tamination could occur because the hydrostatic pressure would force the
reactive liquid into the pores of the structure. However, this method has
inherent liabilities in that it is only applicable to structures that can
withstand the high pressures generated and also would consume large
quantities of reagents. The applicability of this concept would depend on
the inherent strength of the structure and determination of problems in-
volved in completely sealing the structure openings.

7.4.8.3 Decontaminating Paints

The decontaminating solution may be solubilized in high concen-
tration in a paint which would be applied to contaminated surfaces. A
paint is usually composed of a vehicle (solvent), binders, pigments,
thixotrophic agents (material which liquefies upon stirring but returns to
hardened state upon standing), and drying agents. Since drying would not
be desirable when used to apply decontaminants, the paint should be com-
posed of a mixture of the decontaminating solution, polymeric binders and
a thixotrophic agent. The binder serves to increase the paint viscosity
while the thixotrophic agent would help develop a three dimensional net-
work. When undisturbed, the paint would have a high viscosity and stay in
place after it had been applied. However, under sheer conditions (spray-
ing or brushing) the paint would have a reduced viscosity and therefore
attach uniformly to the wall. The paint vehicle could be either water or

a polar organic solvent which solubilize decontaminants. The solubilized decontaminants would migrate from the paint layer into the building material to cause decontamination of agents. The following are some commercial, water-soluble polymeric binders and thixotrophic agents which may be used:

Latices

Acrylic emulsions such as Rhoplex AC-1533, AC 1062, Experimental
   Emulsion E-1561
Vinyl emulsions, particularly the ones having vinyl alcohol as a
   major component
Ethylene acrylic acid or ethylene methacrylic acid
Copolymers with high acrylic acid content

Water-soluble polymers

Polyvinyl pyrollidone (W. R. Grace)
Vinyl ether copolymers (W. R. Grace)
Polyacrylamide (American Cyanamid)
Polymethacrylamide (American Cyanamid)
Acrylic acid copolymers such as Acrysol WS-68 (Rohm and Haas)
Styrene maleric anhydride salts (Scripsol resins) (Monsanto)
Cellulose derivatives such as starch and modified starch
   Jaguar J2SI, Jaguar Plus, Jaguar 800
   Polymer 705 D, Starchan, Starch Dextrin
   (Stein Hale and Company)
Hydroxyethyl cellulose (Natrosol 250, Hercules)

Thixotrophic agents

Carboxymethyl cellulose

Hydroxyethyl cellulose

Finely divided silica such as Sylox (W. R. Grace)

Synthetic colloids such as Baker Thixicin R, Thixicin GR,
    Thixicin E, Carbopol 934, 940, and 941

7.4.8.4 Absorbing Layers (Gels)

A number of polymeric materials have the ability to hold many times their weight in water. In general these compounds (hydrogels) are highly carboxylated cellulose and acrylic polymers which contain cross-linking functionality to maintain their mechanical integrity in the highly swollen state. Solutions or dispersions of these polymers may be sprayed on the contaminated surface and allowed to dry. The aqueous decontamination solution would be applied next. Amounts of decontaminant solutions on the order of 360 grams of water per square foot of surface may be absorbed by these hydrogels, e.g. Waterlack A-175 from Grain Processing Corp., Iowa.

A crosslinked (thermoset) coating would be applied if non-aqueous solvent is used for the decontaminating agent. The decontaminating agent would be dissolved in a solvent which has high swelling ability towards the coating resin.

When the decontaminating solutions are sprayed over the absorbing layer they would be held in place and allowed to diffuse and migrate into the building materials.

7.4.8.5 Cellular Structures (Foams)

Polymeric solutions will foam and form a cellular coating when sprayed on a surface. This is generally performed by dissolving volatile

liquids or gases in the polymeric solutions which are evolved when the spray impacts with the surface. Polymeric materials which may be used for foams are hydroxymethyl celluloses, polyurethanes and urea-form aldehyde resins. By choosing the appropriate base resin (polymer), foaming agents and surface active additives, foams can be produced which contain closed or open (interconnecting) cells and which have various "skin" thicknesses. The ideal foam for decontamination purposes would have open cells and a thin skin (or no skin at all). The decontaminant solution could be mixed with the foaming solution. Alternatively, the decontaminating solution could be applied after the foam had already been sprayed on the wall. In either sequence the open cell structure would be filled by decontaminant solution in large quantities. The decontaminating solutions would be able to migrate into the building material.

7.4.8.6 Barriers

Barriers are external, impermeable layers which will prevent the evaporation of liquid decontaminants or solvent into the building environment and thereby will direct the diffusion of decontamination liquids into the building matrix. Barriers will be particularly useful when heating is applied to increase decontamination rates and to enhance the internal diffusion of the reactant system. Barriers may be applied when reagents are applied directly as liquid films or are incorporated in any of the various retention concepts described above. Possible barriers include plastic films or metal foil which would be mechanically attached. Spray-on polymeric backings may possibly be sprayed directly on cellular foam structures to form an effective and tightly sealed barrier.

7.4.8.7 Post-Decontamination Sealant Treatments

Post-decontamination sealant treatments involve a polymeric coating applied to building surfaces which will absorb and decontaminate

agents potentially present in the material matrix after the heat active decontamination procedure has been performed. This activated coating will trap those contaminants which migrate from the structure interior to the surface long after decontamination has been completed. The "new" surface contaminants would then be absorbed and decomposed upon making contact with the active surface coating.

Decontamination of explosives will require that the agents are somewhat soluble in the specific polymer and that reactive moieties are present to initiate decomposition.

The passive treatment coating should be able to absorb and decompose any agent which would migrate to the surface and should contain sufficient reactive capacity to totally decompose the explosives. This coating can be designed to adhere to the surface permanently or to be removed at a later time. Removal may be necessary if the coating is being loaded up with significant amounts of explosives. Studies should be conducted to determine the most appropriate decontaminant to be used in coatings for specific explosives.

7.4.8.8 Removal of Liquids

Three potential techniques could effectively remove used decontaminating solutions and reaction products after the decontamination reaction is completed. Washing, evaporation, and absorption are known techniques for the removal of foreign material from a surface.

Washing can be performed with water, aqueous based solvent systems or other appropriate solvents. The solvent must be matched with the solubilities of the decontamination solutions.

Evaporation may be accomplished with radiation or convection heating. The heating requirements depend on the heat of vaporization of the specific reactive liquid and its boiling point. Natural aeration could also be used for evaporation of solvents and by-products from the structure. Depending on the nature of the reaction product evaporation may leave undesirable residues of nonvolatile components on the structure.

Absorption may be attained by using absorbent such as activated carbon, silica gel, molecular sieves, sand, charcoal, foam films or other polymeric structure, perlite, creped cellulose wadding, diatomaceus or fullers earth, plastic fibers, and porous silica. The optimum absorbent must be determined for the reactive liquid used for the treatment. The absorbent must not be decomposed by the chemicals applied or the products formed.

7.5 DECONTAMINATION CONCEPTS WITH SPECIFIC APPLICABILITY

The evaluation of novel decontamination concepts was based mainly on the potential applicability of the concept to effectively decontaminate the entire building and its contents of explosives. Decontamination concepts that have applicability to a limited portion of the building therefore, tended to receive poorer ratings. A few concepts have been identified, however, that seem to be very well suited for specific applications, especially in situations where it may not be required to decontaminate an entire building with a single decontamination method. In particular, the following concepts have definite potential for specific applicability for decontamination of explosive facilities: Flashblasting, Electropolishing, Supercritical Fluids, and Ultrasound.

7.5.1 Flashblasting

Although Flashblasting is only effective as a surface treatment and is limited mainly to flat surfaces, it does permit rapid paint removal and rapid thermal decomposition of surface contaminants. In situations where a paint coating has effectively provided a penetration barrier, the contaminant residues would be confined predominantly to the surface. Under these conditions, other methods of paint removal may be less desirable compared with Flashblasting for various reasons. Paint stripping solvents would not decompose the contaminants contained on or in the paint layer, and thus a secondary decontamination of the removed paint would be necessary. Also, with porous materials such as concrete and bricks, the

stripping solvent may solubilize surface contaminants and carry them further into the substrate. Abrasive removal of paint layers would result in large volumes of removed paint and spent abrasive requiring further treatment. Paint removal by flaming would be less rapid and have a higher potential for thermal damage and escape of volatiles compared with flashblasting.

Thus, for painted concrete and brick, flashblasting may be a particularly promising decontamination technique.

7.5.2 Electropolishing

Electropolishing has applicability to unpainted metal surfaces only. However, within this constraint, it is potentially a highly effective technique. Small metal objects, such as tools, equipment, etc., can be rapidly decontaminated by remote tank Electropolishing. This method may be more efficient than the commonly employed thermal decontamination procedure. A system for electropolishing the inside of pipes has been developed, and may be particularly applicable to agent contaminated pipes where heating could easily result in escape of toxic vapors.

One disadvantage of Electropolishing is the requirement for purification and treatment of the contaminated electrolyte. This requirement must be considered when comparing Electropolishing with alternate methods.

7.5.3 Supercritical Fluids

The main disadvantage in the use of Supercritical Fluids for decontamination purposes is that the material to be decontaminated must be contained in a pressure vessel. Although it is impractical to place an entire building in a pressure vessel, it may be practical to treat smaller objects in this manner. Unlike electropolishing which can handle metal objects only, Supercritical Fluids could potentially decontaminate all building materials. Thus, it may be feasible to use supercritical fluids for objects made of metals, wood, plastics, rubber and other miscellaneous materials. Another advantage in the use of supercritical fluids is that purification of the contaminated fluid entails merely reducing the pressure and allowing contaminants to settle out.

7.5.4 Ultrasound

Ultrasound tank cleaning has potential applicability for decontamination of small objects and equipment. The cleaning action would be confined primarily to the surface, however. Specially designed hand-held ultrasonic cleaners could be employed to decontaminate large equipment such as steel tanks. Like electropolishing, however, an added requirement in the use of ultrasonic decontaminating is the purification of the contaminated solvent.

7.5.5 Reactive Amines

See Section 7.4.5.4 for details.

7.5.6 Chromic Acid

See Section 7.4.5.5 for details.

8.0 INERTING OF EXPLOSIVES CONCEPTS

8.1 INTRODUCTION

Another objective of this study was to study and evaluate potential concepts for the inerting of explosives in contaminated buildings. The goal of inerting explosives within contaminated buildings was to render the explosives non-explosive so that demolition and disposal of these buildings could be safely performed. The knowledge gained from our site surveys also indicated that an appropriate inerting method must necessarily have minimal potential for fire initiation since some buildings targeted for demolition were located close to operating explosives plants. In considering the utility of various concepts, we make a semantic distinction between the inerting and desensitization potential of concepts towards explosives: Inerting refers to converting an explosive to a non-explosive state after treatment; desensitization refers to reducing the relative explosivity of an explosive from its original magnitude to some lowered (but finite) explosivity as measured by standard explosivity testing methods.

We have identified and evaluated eight concepts which may result in the inerting or desensitization of explosives. One of these concepts "Solubilization and Inerting of Explosives Through Complex Formation" has previously been described and evaluated as a "Combination Concept" which also has utility in the decontamination of explosives. All decontamination concepts which were chosen for experimental validification in Phase II studies will also be considered in terms of their inerting potential during this validification studies.

8.2 EVALUATION OF INERTING CONCEPTS

The inerting criteria scores and total scores that each concept received are shown in Table 28. Total scores ranged from +10 to +1 for

these concepts and Inerting Potential criteria scores ranged from +2 to
-2. Those five candidate concepts which had total scores ranging from +10
to +3 were judged to have significant merit for inerting explosives.
However two of these concepts were not recommended at this time since
their scope of applicability in each case was limited to a narrow range of
explosives. The following three concepts are recommended for Phase II
experimental verification:

        1) Inerting of Explosives By Solubilization

        2) Desensitization of Explosives By Water Treatment

        3) Desensitization of Explosives by Steaming.

These inerting and desensitization concepts are briefly described below.
The most promising concepts are variations of each other in that they in-
volve various degrees of solubilization in the inerting process. All in-
erting and desensitization concepts are described in detail in Appendix
III.

8.3   DESCRIPTION OF INERTING CONCEPTS

8.3.1   Inerting of Explosives by Solubilization

      This concept received a +10 overall score and +2 ratings in both
the Mass Transfer and Inerting Potential criteria. This concept is based
on the well known fact that almost all unstable compounds are safe to
handle when dissolved in solution. It is predicted that solubilized ex-
plosives (except perhaps nitroglycerine) may also be safely handled or
inerted when dissolved in an appropriate solvent.

      The most suitable solvent for explosives solubilization would be
non-flammable, non-volatile and moderately viscous in addition to having a
high solubility for a wide range of explosives. A low volatility would

TABLE 28. CHEMICAL INERTING OF EXPLOSIVES

Criteria	Solubilization	Water Treatment	Amines and Acetone/Acetonit.	Denitration Reactions	Steaming	Reductants	Coatings Stabilizer
Mass Transfer	++	-	++	++	-	-	-
Inerting Potential	++	++	++	++	-	-	-
Safety	++	++	-	-	+	++	+
Applicability to Complex Surfaces	++	++	++	++	++	++	++
Operating Costs	++	++	++	++	++	++	++
Capital Costs	+	++	++	+	+	+	+
Waste Treatment Cost	-	-	-	-	-	-	-
Total/Pre-Screen Total	10/4	8/1	7/4	6/4	3/-2	3/-2	1/-3

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not allow evaporation of the solvent and subsequent deposition of the ex-
plosive (in a hazardous state) at any time between the application date
and final disposal date. A moderate solvent viscosity would allow sig-
nificant residence time on vertical surfaces to allow solubilization be-
fore run-off occurred. Ideal solvent candidates in general are also those
which are mutually soluble in water which would allow the economical use
of that solvent. Water, solvent compositions would also have a lowered
flammability compared to the use of that solvent alone. A variety of
water soluble polymers, surfactants, complexing agents and wetting agents
could also serve as solubilizing agents if a water based solvent system
were employed. Alternately, various oils with or without added solubil-
izing agents could be used to solubilize or significantly wet the explo-
sives. Petroleum oil is claimed by one company to desensitize TNT and is
used privately for TNT building cleanup (Private communication). A sig-
nificant variation, regardless of the composition of the solvent, is to
add chemical decomposition agents which would serve to decompose the sol-
ubilized explosive to a permanently non- explosive state.

This concept earned a +2 rating in the Safety criteria since
solvent compositions may be chosen which would have negligible flammabil-
ities and toxicities.

8.3.2 Desensitization of Explosives By Water Treatment

This concept, which is an intuitatively obvious method towards
the inerting of explosives, would entail the initial wetting and subse-
quent wetting of the explosives with large volumes of water. This concept
is actually a specific variation of the "Solubilization" concept initially
presented. A potential problem with this concept is that all explosives
have a very low solubility in water and therefore may be wet only on the
surface if thick deposits of explosive are present. However various in-
dustrial manufacturers or processors of explosives use water by itself or
as a first step before using steam to daily clean their contaminated

facilities. Surfactants or wetting agents may be used with the water washes. One company uses a high pressure water lance at 600-1200 psi which incorporates polyethoxyphenol as a wetting agent, for a range of explosives (Private communication). A stream of water at 400 psi is employed in the Cavijet process to wash out TNT and Composition B out of unused projectiles (Private communication). RDX (which is claimed to be desensitized when wet) deposits may be removed by first wetting and then flushing with copious amounts of hot water (Private communication). Nitrocellulose is claimed not to be classified as an explosive when it has been well wet with water (Private communication). However if the time delay between water treatment and demolition were significant, the inerted nitrocellulose could dry out and be converted back to an explosive compound. For this reason, demolition would be required to proceed immediately after wetting occurred if this concept were to be safely applied. These processes dissolve only a small amount of the explosive but partially serve as a mechanical transport system to move the desensitized explosives to sumps where they can be removed and treated further.

This concept received an overall score of 8 and a Mass Transfer score of -1 and an Inerting score of +2 since explosives have low solubilities in water but some explosives are claimed to be totally wetted by inerting. The method appears to have significant merit as an explosive treatment method prior to decontamination, especially if a water lance is used in conjunction with surfactants, wetting agents, complexing agents, or cosolvents which would help solubilize and remove even bulk quantities of explosive from the building. The complete run-off would need to be collected and the explosives decontaminated after collection.

8.3.3 Desensitizations of Explosives by Steaming

As mentioned in the previous concept on "Water Treatment", steam may be used after an initial water wash to transport explosives to a sump. Steam may also be used without prior water washing to migrate TNT, RDX and

HMX from contaminated surfaces to sumps (Private communication). One claim has been made that TNT may be inerted to a non-explosive state by the successive applications of steam, kerosine, and steam. However, a warning was also noted that Tetryl may detonate in the presence of steam (Private communication). Two concept description forms entitled "Manual • Steaming" and "External Steaming" are found in Appendix III of this report.

This concept may be considered to be a variation of the previous "Water Treatment" concept but it was still evaluated. This concept may coincidentally result in desensitization or inerting of some explosives but its potential role is assumed to involve the mechanical transport of explosives from the deposition site to a sump. This concept received a +3 overall score and a -1 rating score in both the Mass Transfer and Inerting Potential criteria.

8.3.4 Decomposition of TNT With
Reactive Amines and Acetone or Acetonitrile

This chemical decontamination concept, which has previously been described was not chosen for Phase II verification as a decontamination concept partly because potentially toxic products were expected to be formed and this concept is known to be applicable for TNT and tetryl only. This concept received a +7 overall score and received +2 rating in both the Mass Transfer and Inerting Potential criteria. As previously described this concept has the potential for safely decontaminating bulk amounts of TNT. However, all the reactant systems which have been studied include chemicals which are highly flammable which led to a -2 rating in the Safety criteria for this concept. However, it is feasible that related non-flammable reactant systems can be developed which would lead to effective decomposition and inerting of TNT. The flammability of this concept could also be significantly reduced by the utilization of gels or foams with or without backing materials. However, due to the flammability

hazards and limited scope of explosives, this method is not recommended for further verification at this time.

8.3.5 Inerting of Nitrocellulose By Denitration Reactions

This concept received a +6 overall score and +2 rating scores in the Mass Transfer and Inerting Potential criteria. This concept includes a number of reactions which are known to cleave the nitro groups from various explosives. The percent nitro group removal from nitrocellulose which is required to render this explosive inert is not known, but various reactions are available which can result in a high degree of nitro group removal. The denitration reactions in this concept primarily involve amines which may be applied neat or dissolved in organic solvents. The fact that nitro group displacement is reported to be catalyzed by copper salts (Muraour, 1936) indicates that copper (and other) catalysts may also effectively catalyze the other denitration reactions.

The use of organic solvents or neat amines in the reactions employed in this concept is required to initiate the swelling of nitrocellulose which must occur before nitrocellulose which must occur before nitrocellulose can be solubilized. Since these flammable organic reactants may be required for solubilization, this concept was given a -2 rating for the Safety criteria. However if these reactions will still occur upon dilution with water or using less flammable amines the Safety rating would be increased. Alternately the use of gels or foams with backing material would significantly lower the flammability potential and increase the Safety rating. Since this concept has a significant flammability hazard and is limited primarily to nitrocellulose and potentially nitroglycerine, this method is not recommended for further verification at this time.

8.3.6 Desensitization of Explosives With Various Reductants

A variety of explosives may be desensitized by exposure to aqueous solutions of a variety of reductants such as oxalic acid, formic

acid, urea, hydrazine, dimethyl hydrazine, etc. (Roth, 1978). This con-
cept received a -1 rating in the Inerting Potential criteria which indi-
cates that the explosives were not inerted by this process but still had
some residual explosivity (i.e., they were desensitized). Since the ex-
plosives still has significant explosivity (as measured by drop tests)
this concept is not recommended for further study in the inerting of
buildings prior to demolition.

8.3.7 Desensitization of Explosives With Stabilizer Coatings

Various stabilizing coatings have been applied to military ex-
plosives to decrease their sensitivity to detonation. Examples of sta-
bilizing agents include waxes, carbowaxes, organic dyes and specific com-
pounds such as saligenin. These materials are typically applied in a
uniform manner during the manufacture and processing of the explosive.
However the coated explosive still has a high explosivity since it will
obviously be used in this state as a military explosive. This concept
received a -2 rating in the inerting potential which indicates that the
explosive is not expected to be desensitized at all when applied non-
homogeneously from the exposed side of the explosive deposit. This con-
cept is not recommended for further study for the inerting of buildings
prior to demolition.

8.4 DEMOLITION

Demolition is a widely utilized method for building removal.
Demolition techniques include the use of explosive blasting, wrecking
balls, front end loaders and manual methods such as pneumatic hammers,
etc. The method has applicability to all types of building constructions.
Demolition may be particularly suited (cost effective) for the selective

excessing of 1940's vintage manufacturing buildings because there is
little or no applicability of these buildings to other uses. In the case
of buildings contaminated with explosives, mechanical demolition may re-
sult in an explosion if high concentrations of explosive residues are en-
countered. This has been demonstrated to be a real hazard based on in-
formation obtained from the Site Surveys. For example, at Sunflower Army
Ammunition Plant a worker was killed when he attempted to remove a NC tank
which had been supposedly 3X decontaminated but exploded when his cutting
torch contacted the metal. Other examples could be cited where non-
flaming demolition methods have resulted in explosions. Thus, the feasi-
bility of demolition techniques is primarily dependent on the effective
inerting of all contained explosives.

9.0 DECONTAMINATION OF WHITE PHOSPHORUS

9.1 INTRODUCTION

Methods to be used for the decontamination of facilities used to
load munitions with white phosphorus are to be considered. Unless white
phosphorus is covered with water to exclude air it spontaneously ignites
and burns to form primarily phosphorus pentoxide. Because of this reac-
tivity it was judged that white phosphorus would exist only in areas where
air has been excluded or at the bottom of water pools. Such areas would
include phosphorus storage tanks, drain traps and sumps where a layer of
water is assumed to have been maintained to prevent contact of the phos-
phorus with air. Piping, pumps, etc. are usually sealed by valves so
sufficient air may not have been present to decompose all of the white
phosphorus. Since phosphorus freezes at 44 C, almost all piping and
valves used to conduct the phosphorus can be heated to maintain it in the
liquid state.

Water covering elemental phosphorus gradually becomes acidic.
The phosphorus that dissolves in the water gradually oxidizes to form the
various phosphorus oxides which hydrolyze to produce acids. This acidic
solution is commonly called "phossy" water in the phosphorus manufacturing

industry. A concept to treat white phosphorus contaminated facilities or
equipment must involve methods which can act through the aqueous phase.
The material surfaces to be treated are metal or concrete.

A current disposal practice used by the white phosporus manu-
facturing industries is to return phossy water and related sludges to the
elemental phosphorus manufacturing processes. Gross amounts of phosphorus
are removed from equipment, tanks, etc., by the use of steam lances with
entrained air but the fumes of P_2O_5 are excessive. Pipes and other
vessels destined for salvage are cut up with a torch and the phosphorus
allowed to burn in the open.

At one army arsenal, phosphorus-contaminated metal that is to be
scrapped is cut up and allowed to burn in the open. Metal parts to be
reused are washed down with steam, detergent and 165 F water. The phos-
phorus laden water is collected in tanks and treated with ozone. The acid
solution is neutralized and then spray dried.

9.2 CONCEPTS FOR DECONTAMINATION OF WHITE PHOSPHORUS

Four concepts for the decontamination of white phosphorus con-
tamination were considered. These are briefly discussed below. Detailed
descriptions are provided in Appendix III.

9.2.1 Air Entrainment

Water, supersaturated with respect to dissolved oxygen by in-
creasing the air (or oxygen or ozone) pressure to 50 psi, is injected into
the cavity or vessel containing the water-covered phosphorus. Phosphorus
would be oxidized to the water soluble oxy-acids and then pumped out. The
rate of oxidation would be large enough to raise the temperature of the
solution to above the melting point of phosphorus which would thereby im-
prove the reaction rate. The oxygen could be supplied as a solution of
hydrogen peroxide as well. The reactions that can take place are as

follows:

$$P_4 + 5O_2 + 6H_2O \longrightarrow 4H_3PO_4$$
$$10H_2O_2 + P_4 \longrightarrow 4H_3PO_4 + 4H_2O$$
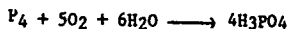
Advantages

o The process is inherently simple to implement and execute.

o Chance of fire is minimized.

o Surface clean up requires only neutralization and a water rinse.

Disadvantages

o Acid solutions will corrode metal parts.

● High oxygen partial pressures, interacting with large pockets of elemental phosphorus can create P_2O_5 fume above the water surface.

9.2.2 Cupric Sulfate Solution

In very old elemental white phosphorus production plants, copper sulfate solutions were used for first aid in case elemental phosphorus came in contact with a worker's skin. The copper in solution reacts to form solid copper phosphide or elemental copper on the surface of the phosphorus so as to keep air from coming in contact with it. The reactions that are possible include:

$$3P + 3CuSO_4 + 6H_2O \longrightarrow Cu_3P + H_3PO_3 + 3H_2SO_4$$
$$2P + 5CuSO_4 + 8H_2O \longrightarrow 5Cu + 2H_3PO_4 + 5H_2SO_4$$
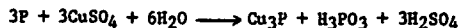
Any elemental phosphorus contamination on the surface of the vessel or in suspension in the phossy water would be coated to prevent air attack. It would then have to be removed from the surface and disposed.

Advantages

● The process involves an existing art for controlling the air oxidation of elemental phosphorus.

● The product is a solid which could be handled in air.

Disadvantages
o The solid product will deposit on solid bulk phosphorus and limit reaction to the surface.
o Thick deposits and subsurface phosphorus would exhibit limited reactions.
o Complete phosphor s r. noval requires attretion and scouring to expose fresh p osphoius.
o Waste disposal would require treatment of copper, soluble copper salts, copper phosphide and acids.

9.2.3 Hyphalogenite Solutions

Alkaline calcium and/or sodium hypochlorite or hypobromite solutions will oxidize elemental phosphorus to phosphate ion. The hypochlorite ion is a very strong oxidant. For example, if sodium hypochlorite were used, the reaction would be

$$12NaOH + 10NaOCl + P_4 \longrightarrow 4Na_3PO_4 + 6H_2O + 10NaCl$$

This reaction is pH sensitive. Under slightly acid conditions the hypochloride solution would decompose into chlorine. If the system becomes too alkaline then, the potential for phosphine formation exists.

Advantages
o This reagent is readily available and a familiar Army decontamination material which converts elemental phosphorus to the water soluble phosphate ion.
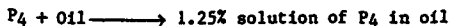
Disadvantages
o Reagent releases chlorine in acidic solutions. If calcium hypohalogenite is used, insoluble calcium phosphate will yield sludge.
o The reagent causes corrosive action on metals.

o Waste disposal requires removal of excess hypochlorite ion
   from solution or sludge.

9.2.4 Mineral Oil Emulsion

Phosphorus is soluble in mineral oil. An emulsion of mineral
oil and water would be circulated through a cavity or other contaminated
structure to become laden with white phosphorus. The laden emulsion would
be aerated outside of the cavity to convert the phosphorus oxy-acids
releasing the oil for recycle. The process probably would involve the
following steps

$$P_4 + Oil \longrightarrow 1.25\% \text{ solution of } P_4 \text{ in oil}$$

$$Air + P_4 \longrightarrow H_3PO_4 + \text{phase separation}$$

Disposal of wastes would be performed by neutralization with lime and
disposal in a landfill. Some oil may be occluded in the wastes from the
oil emulsion treatment.

Advantages
o Phosphorus is removed without chemical action (physical
   removal).
o Conversion to phosphoric acid occurs in separate reactor and
   not in phosphorus-contaminated vessel or cavity.

Disadvantages
o Treatment leaves phosphorus laden oil on surface which will
   require additional treatment.
o Solvent and oils are combustible.
o Foam can form as a sludge which contains oil.

9.3 CONCEPT EVALUATION

The concepts were rated for the criteria used to evaluate chem-
ically oriented explosive decontamination concepts. The results of the

evaluation are summarized in Table 29. The water-entrained air concept scored the highest and is recommended for evaluation in Phase II studies.

Air Entrainment

Water, supersaturated with air, is injected into a cavity and continuously pumped out and collected for treatment or recycle. As the process proceeds and acid concentration increases a bleed stream would be neutralized and then added to the installation water treatment facility for disposal as a phosphate salt in solution. The reaction would be expected to be controllable by the amount of air introduced to the cavity thereby reducing chances for formation of a P_2O_5 plume. Since hydrogen peroxide, oxygen and ozone are probably equally effective reagents, their presence can be used to reduce recycle requirements. The process can be monitored by changes in the acid content of the outlet stream. The principal product from the reaction will be phosphoric acid with the possibility of the presence of the lower oxy-acids of phosphorus. If air, oxygen or ozone were used, no treatment of the waste stream other than neutralization would be required. If hydrogen peroxide were used, the excess would have to be decomposed. Neutralization with sodium alkali bases (Na_2CO_3, NaOH etc.) would lead to water soluble wastes whereas treatment with lime would yield a sludge that would have to be dried and then land filled.

Even though hazards from fire are ever present with phosphorus, the water flooding method would tend to minimize it. If metal parts are being treated, excessive acid levels could lead to hydrogen evolution by acid attack of the metal.

Phosphorus contamination that has penetrated into porous material and to some extent metals would be difficult to treat with water-air emulsions. However, the extent of this type of contamination is now known. If concrete storage tanks or sumps exist, penetration of phosphorus into cracks is likely because of its low viscosity at 50 C when saturated with water.

TABLE 29. WHITE PHOSPHORUS DECONTAMINATION CONCEPTS EVALUATION

Criteria Evaluated	Air Entrainment	Hypohalogenites	Cupric Sulfate	Mineral Oil
Safety	++	-	+	-
Damage	++	++	++	++
Penetration	-	-	-	—
Complexity	++	++	++	++
Operating Cost	++	++	+	+
Capital Costs	++	++	++	+
Waste Treatment	+	-	—	+
TOTALS	+10	+5	+5	+4

10.0 COST ANALYSIS

A preliminary cost analysis was performed on those concepts
which passed the screening procedures. Since the costs for the chemical
concepts will be similar because of similar application methods, a generic
cost was calculated and assumed to be representative of all chemical con-
cepts including the selected white phosphorus decontamination concept.
The selected desensitization concept was costed assuming the building is
demolished following inerting.

A summary of the estimated costs of the selected concepts is
given in Table 30. These costs were based on the decontamination of the
three structures described in Section 6.3. Detailed cost breakdowns are
given in Appendix II. It is important to note that in all concepts,
further information is required to make a detailed cost analysis. The
figures provided in Table 30 are only order-of-magnitude estimates. Thus,
at this time, it does not seem appropriate to eliminate any concepts on
the basis of cost.

TABLE 30. THERMAL, ABRASIVE, AND EXTRACTION CONCEPTS COST SUMMARY[a]

Concept	Operating Cost in (1000$)	Capital Cost in (1000$)	Total Cost in (1000$)
Hot Gases	$ 76	$45	$127
Infrared Heating	$105	$88	$193
Hydroblasting	$149	$93	$242
RadKleen	$145	$45	$190
Steaming (External)	$ 78	$11	$ 89
Vapor Circulation	$154	$29	$183
Liquid Chemical Reactants	$ 83	$ 9	$ 92
Sandblasting	$ 95	$30	$125
Vacu-blasting	$124	$35	$159
Desensitization/Demolition	$195	$46	$242

(a) In 1982 $

11.0 ANALYTICAL RESULTS

11.1 OBJECTIVE

Analytical research support undertaken during this project was directed toward certification of previously developed methods for analysis of explosives on building materials. These methods included work done by both Midwest Research Institute (Lakings, 1981) and A. D. Little, Inc. (Goodwin, 1982) as well as techniques developed originally by Battelle-Columbus Laboratories for USATHAMA (USATHAMA Certified Methods Nos. 1K, 1L. 3F, 3S, 3V, and 4B). The goal of this analytical task was to provide method certification in accordance with USATHAMA guidelines for six explosives on six building materials.

11.2 EXPERIMENTAL APPROACH

Explosives used during analytical method certification were 2,4-dinitrotoluene (2,4-DNT); 2,6-dinitrotoluene (2,6-DNT); 2,4,6-trinitrotoluene (TNT); 2,4,6-trinitrophenylmethylnitramine (tetryl); cyclotrimethylenetrinitramine (RDX); and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). Building materials selected for use were unpainted and painted samples of stainless steel, mild steel, and concrete. These samples were painted with an enamel alkyd paint, which was selected as representative of paint likely to be encountered at explosive contaminated facilities. In addition, an alkyd paint was expected to present a greater challenge to extraction and recovery of an explosive than would a latex paint. Specifications on the building materials and paint are given on the method certification write-up, which is included as Appendix IV.

The basic procedure that was developed for recovery of explosives from surfaces (Goodwin, 1982) involves extraction of the contaminated samples using acetonitrile as the extraction solvent and sonifica-

tion to facilitate intimate contact between sample and solvent. This procedure was developed for an assortment of explosives and a variety of unpainted surfaces. The procedure had not included the explosive HMX and was never tested with painted surfaces. Method certification by Battelle was extended to include HMX and painted samples.

Instrumental analysis of explosives following recovery from the surface sample was accomplished by linear gradient high performance liquid chromatography (HPLC). HPLC has been used successfully for these explosives and provides a convenient means for analysis because difficulties encountered by other techniques, such as gas chromatography, with thermal degradation and on-column reactions are avoided.

11.3 RESULTS

Extraction, recovery and analysis of the six explosives were conducted successfully for the three unpainted building materials. This success during method certification is notable in that HMX had not been attempted previously during method development by A. D. Little and Midwest Research Institute (Lakings, 1981; Goodwin, 1982). Five of the explosives were successfully recovered and analyzed from the painted materials. However, recovery and analysis of a sixth explosive, RDX, were unsuccessful due to the presence of a component extracted from the paint. This component eluted at the same relative retention time as RDX and prevented isolation of the peak for RDX. Subtraction of the peak for this interference was also attempted using the method blanks; however, the amount of this component that was extracted was apparently random and could not be quantified. Sample chromatograms for unpainted and painted method blanks and for a calibration standard solution are presented in Figures 16 through 18. As shown by Figure 18, the HPLC instrumental parameters used allowed simultaneous resolution of all six compounds. These instrumental conditions were selected on the basis of prior Battelle methods developed for USATHAMA (USATHAMA Certified Methods No. 1K, 1L, 3F, 3S, 3V, and 4B),
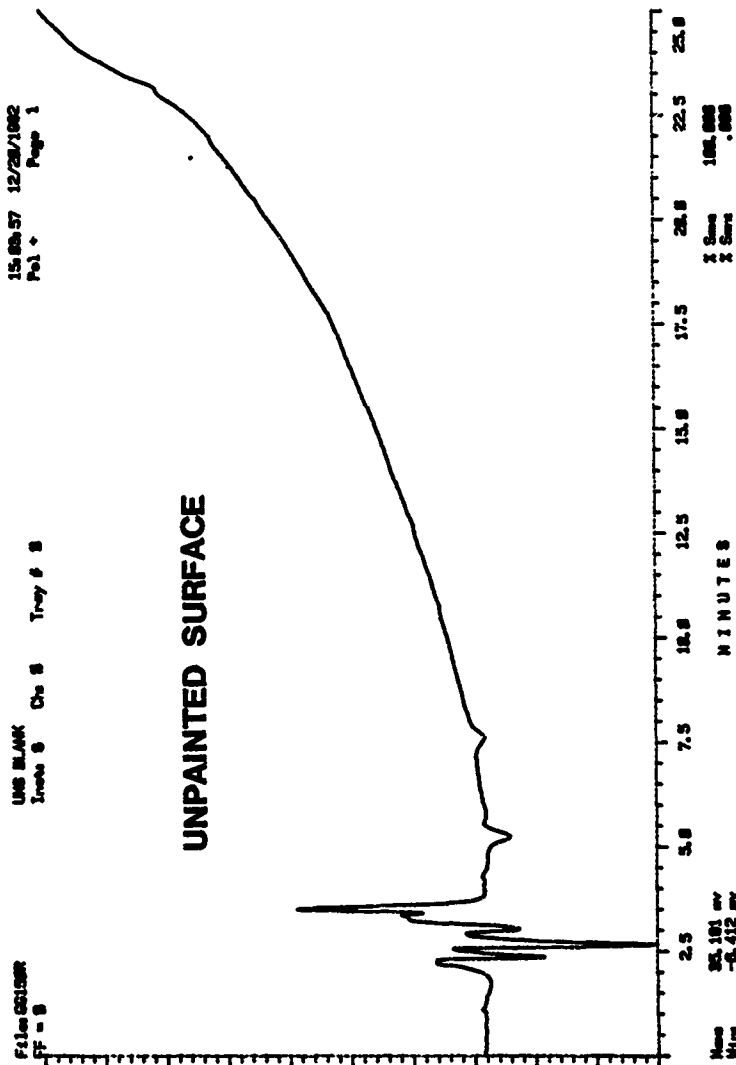
FIGURE 16. CHROMTOGRAM FOR HPLC ANALYSIS OF METHOD BLANK OF AN UNPAINTED
MILD STEEL SAMPLE

PAINTED SURFACE

File: GG151R
FF = 0

PMS BLANK
Inets 0   Chn 0   Tray # 0

15:45:02 12/20/1982
Pol +   Page 1

Name   57,021 mv   % Sens   100,000
Wire   5,055 mv   % Sens   .000

M I N U T E S

2.5   5.0   7.5   10.0   12.5   15.0   17.5   20.0   22.5   25.0
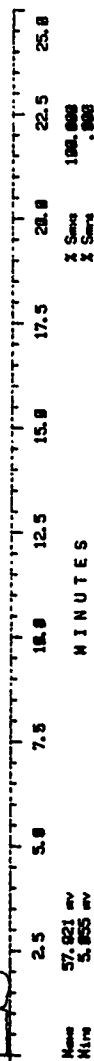
FIGURE 17.   CHROMATOGRAM FOR HPLC ANALYSIS OF METHOD BLANK OF A PAINTED MILD
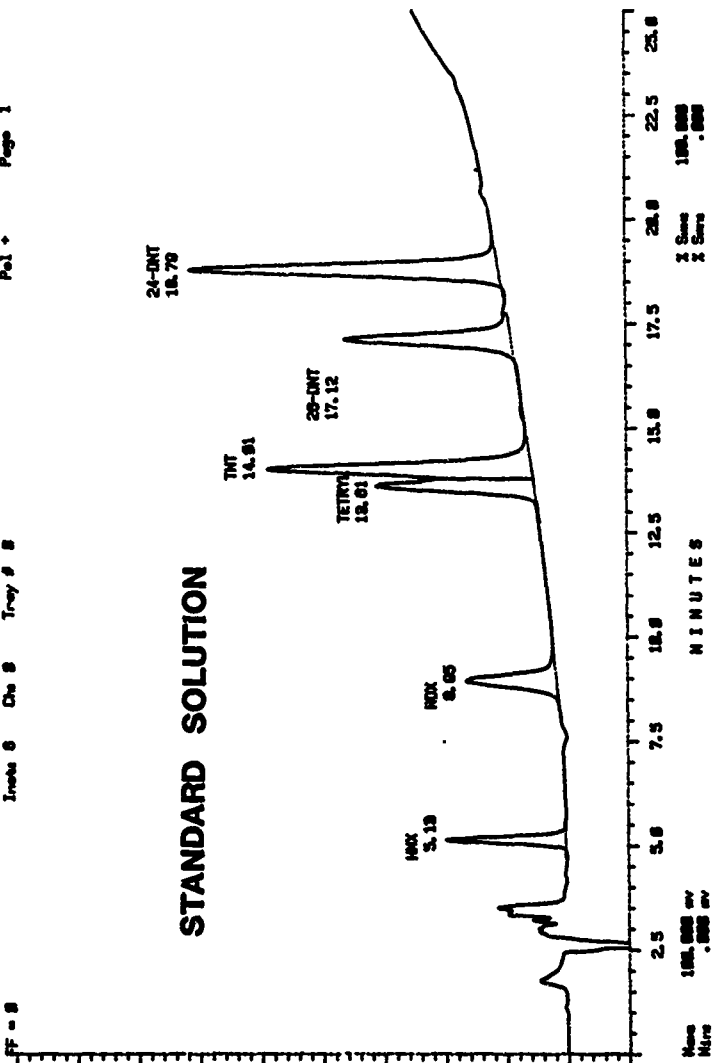STEEL SAMPLE

FIGURE 18. CHROMATOGRAM FOR HPLC ANALYSIS OF A STANDARD SOLUTION CONTAINING
40.0 µg/L OF EACH EXPLOSIVE

because the conditions reported by A. D. Little (Goodwin, 1982) both did not include HMX as an analyte and required separate analysis for 2,6-DNT from that done for other explosives.

Sample chromatograms for method blanks and spiked samples on all six materials are given in Appendix V. Detection limits for each combination of explosive and building material are given in Table 1 of the method certification write-up (Appendix IV).

In summary, method certification was successfully conducted on 33 combinations of explosive and building material. This figure exceeds the task goal of 25 combinations of explosive and material. A single set of HPLC operating parameters provided simultaneous resolution, of 2,4-DNT; 2,6-DNT; TNT; Tetryl; RDX; and HMX. The sample preparation procedure developed previously (Goodwin, 1982) was extended successfully to include both the explosive HMX and the use of painted surfaces.

12.0 RECOMMENDATIONS

The following concepts for the decontamination and inerting of explosives and the decontamination of white phosphorus are recommended for experimental verification in Phase II studies.

12.1 EXPLOSIVES DECONTAMINATION

12.1.1 Thermolysis Concepts

The Thermal Decomposition by Hot Gases and Thermal Decomposition by Radiant (Infrared) Heating concepts were the two highest ranked thermal concepts. However, only the Hot Gases concept is recommended for evaluation in the Phase II studies. The combination concept entitled Deactivation of Explosives During Thermolysis by Radical Trapping will also be studied in conjunction with this thermal concept since it provides a potential method to deactivate sensitive explosives and allow their safe thermolysis. The Infrared Heating concept was rated almost as high as the Hot Gases concept but is not recommended for testing since it does not penetrate to depths below the surface as readily as hot gases are expected to.

12.1.2 Abrasive Concepts

The top rated abrasive concepts (Sandblasting, Hydroblasting and
Vacu-Blast) are not being recommended for evaluation in Phase II studies
since the various removal depths that can be obtained for these abrasive
techniques are known. The feasibility of these concepts will be deter-
mined when actual or predicted depth profiles of explosives in contam-
inated buildings become available.

12.1.3 Extraction Concepts

The highest rated extraction concepts are entitled Removal by
RadKleen, Vapor Phase Solvent Extraction, and Steam Cleaning. We recom-
mend that feasibility studies of the first two concepts be combined by
performing vapor condensation extraction studies with various freons
(which would simulate the RadKleen concept) as well as other solvents. A
key knowledge gap in extraction concepts which will be studied is the ef-
fectiveness of solvent mass transfer into and out of porous materials. We
recommend that further information concerning Steam Cleaning be collected
by further consultation with explosives industries that use this technique
for decontamination of their facilities. Further information concerning
Steam Cleaning will also be gathered from the Task 3 verification studies
of this technique for the decontamination of agents.

12.1.4 Chemical Concepts

The following are the highest ranked chemical concepts: Radical
Initiated Decomposition of Explosives, Base Initiated Decomposition of
Explosives and Sulfur Based Reduction of Explosives. We recommend that
each of these concepts and their variations be subjected to an initial
prescreening whereby the percent decomposition of all explosives versus
treatment times and the nature of decomposition products be determined in

solution under conditions which are as similar as possible to each other. Only the concepts which are ranked highest in the prescreening tests will be evaluated further in the Phase II Test Plan.

The combination concept Solubilization and Inerting of Explosives through Complex Formation is also recommended for Phase II study since enhanced solubilization directly relates to the effectiveness of most chemical decontamination and certain extraction concepts.

12.2 EXPLOSIVES INERTING

The top rated explosives inerting concepts are based either on the solubilization or wetting of explosives. Three concepts which have significant overlap with each other are: Inerting of Explosives by Solubilization, Desensitization of Explosives by Water Treatment, and Desensitization of Explosives by Steaming. The first two concepts are recommended for evaluation in the Phase II studies. The concept desensitization by Steam is related to the extraction concept entitled Steaming and will be evaluated primarily by consultation with explosives industries that use steam for the simultaneous cleaning and desensitization of explosives.

12.3 PHOSPHORUS DECONTAMINATION

The concept Yellow/White Phosphorus Decontamination Using Water-Entrained Air is recommended for evaluation in Phase II studies.

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1 5 SEP 2006

MEMORANDUM TO Mr. Larry Downing, Defense Technical Information Center, 8725 John J. Kingman Road, Ft Belvoir, VA 22060-6218

SUBJECT: Downgrading from Limited Distribution to Unlimited Distribution

1. The following documents were reviewed, and it was determined by our Technical POC, Mr. Marty Stutz, that the distribution statement should be changed from limited to unlimited distribution.

   a. AD Number: ADB073052: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase I. Identification and Evaluation of Novel Decontamination Concepts. Volume 1.
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   b. AD Number: ADB073034: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase 1. Identification and Evaluation of Novel Decontamination Concepts. Volume 2.
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   c. AD Number: ADB093506: Development of Novel Decontamination Techniques for Chemical Agents (GB, VX, HD) Contaminated Facilities. Phase II. Laboratory Evaluation of Novel Agent Decontamination Concepts.
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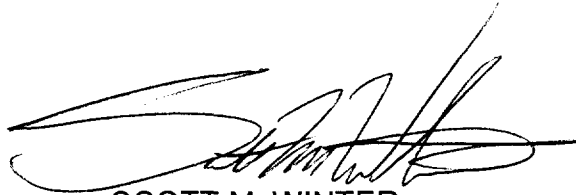
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FOR THE COMMANDER

SCOTT M. WINTER
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Security Officer